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Tailoring water stability of cellulose nanopaper by surface functionalization†

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Cellulose nanopaper (CNP) features appealing properties, including transparency, flatness, a low thermal expansion coefficient and thermal stability, often outperforming conventional paper. However, free-standing crystalline cellulose films usually swell in water or upon moisture sorption, compromising part of their outstanding properties. This remains a major problem whenever working in a water environment is required. Freestanding cellulose nanopaper is prepared by solution casting water suspensions of cellulose nanocrystals with an average width of 10 nm and an average aspect ratio of 28, isolated from Avicel by acid hydrolysis and extensively characterized by AFM and FE-SEM measurements and GPC detection of their degree of polymerization. We demonstrate by elemental analyses, FT-IR, Raman spectroscopy, XRD measurements and water contact angle detection that wet treatment with lauroyl chloride results in surface hydrophobization of nanopaper. The hydrophobized nanopaper, C₁₂-CNP, shows a more compact surface morphology than the starting CNP, due to the effect of chemical functionalization, and presents enhanced resistance to water, as assessed by electrochemical permeation experiments. The new hydrophobized nanopaper is a promising substrate for thin film devices designed to work in a humid environment.

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Introduction

Natural materials are often composites comprising polymeric and/or ceramic components, with a complex hierarchical architecture that results from evolution and spontaneously forms under mild conditions.¹ Among them, cellulose represents the most abundant organic polymer on Earth and is easily accessible and cheap, as it is synthesized by plant cells and bacteria. Cellulose displays attractive potentialities for new technological

applications due to its spontaneous assembly in crystalline fibrils.² Although early reports of Ramby³ and Battista *et al.*⁴ clearly evidenced the possibility of performing acid digestion on cellulose, thereby isolating crystalline nanoparticles, only in the last decade nanocrystalline cellulose has attracted interest of different industries and the scientific community. This recent interest stems from its appealing features such as high tensile modulus, high specific surface area, biodegradability, biocompatibility and sustainability.^{2,5,6} Cellulose nanocrystals (CNCs) are crystalline fibres featuring a high aspect ratio with a diameter ranging from 5 to 50 nm and a length between 100 and 500 nm.⁷ CNCs are appealing in different scientific fields like the manufacturing of nanocomposites⁸ and hydrogels,⁹ drug delivery,¹⁰ biocatalyst immobilization,¹¹ biosensors¹² *etc.* In particular, the intriguing perspective of using nanocellulose-based free-standing thin films, called cellulose nanopaper (CNP) for flexible electronics,¹³ has attracted much attention.¹⁴ CNP represents an ideal substrate for electronics, whose actual challenges are not only flexibility, but also biocompatibility and a straightforward miniaturization. High throughput, cheapness, disposability, transparency,¹⁵ biodegradability and biocompatibility are the pros that make CNP-based scaffolds extremely appealing. Furthermore, CNP-based thin films can display cholesteric chiral nematic ordering from which additional interesting optical properties arise;¹⁶ further properties such as a low thermal

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expansion coefficient, a wide compatibility with several thermal treatments, low surface roughness and good mechanical properties, yield even more versatile thin-films.¹⁷ The CNP-based scaffolds meet the majority of specific requirements for printed electronics and biosensors, in fact scientific reports on the fabrication of electronic devices have appeared in the last years.^{18–24} Fungal degradation of CNP for flexible transistors has also been demonstrated.²⁵ Even though deep knowledge on CNP has been gained, a rather overlooked issue is the water stability.²⁶ For instance, Zhou *et al.*^{19a} have reported complete dissolution of the CNP-based substrate of a solar cell upon immersion in water for 30 minutes. Nanopaper is indeed a hydrophilic material due to the presence of surface free pending hydroxyl groups belonging to the β -D-glucopyranosidic rings composing the cellulose polymer chains. Water can hardly penetrate the cellulose crystalline structure,²⁷ which is very cohesive due to the effect of the cooperative and ordered interchain H-bond interactions, but it can easily leak in the cracks and spaces between the nanocrystals, resulting in an overall swelling and a subsequent dissolution of the nanopaper in aqueous media. Because of the above reasons, this issue can be safely considered a hot-topic for the successful fabrication of electronic devices coupled to aqueous media, and only the recent literature has started to consider this problem.²⁸ For this purpose, CNP should be converted in a water repellent material by chemical functionalization. In connection with our studies on new materials for organic electronics,²⁹ we prepare self-standing thin films of CNP by solution casting of an aqueous suspension of cellulose nanocrystals and tailor their surface with lauroyl ester groups. This functionalization is achieved by a traditional alcohol esterification reaction and carried out by dipping the nanopaper in dichloromethane in the presence of acyl chloride. We attain C₁₂-CNP that presents a functionalized surface, featuring a surface layer of pendant lauroyl ester groups, which are hydrophobic. We demonstrate that the reaction has little influence on the bulk crystallinity of the nanopaper, attaining a very low cellulose degree of substitution by our wet treatment. The potential release of the acyl units as lauric acid to the environment may preserve nanopaper environmental harmlessness. The high stability against water over time of C₁₂-CNP with respect to the untreated nanopaper is successfully demonstrated by electrochemical investigation.

Results and discussion

Preparation and characterization of cellulose nanocrystals (CNCs)

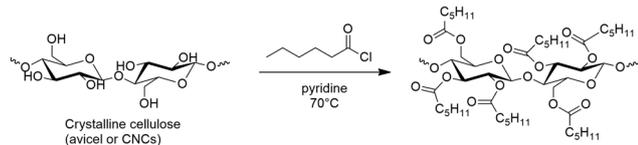
Nanocrystalline cellulose was isolated by acid hydrolysis of Avicel PH-101, a cotton linter-based commercial stationary phase for column chromatography. Avicel PH-101 is composed of microcrystalline cellulose whose particles have an average size of $45 \pm 5 \mu\text{m}$, as judged from optical microscope analyses (see the ESI,† Fig. S1). The acid hydrolysis was carried out in H₂SO₄:deionized water 1:1 v/v at 45 °C for 80 minutes (see the ESI† for details on reaction yield and screening of reaction conditions). After purification, the reaction produced a suspension of crystalline materials in water at pH 7. The crystals were kept suspended by surface negative charges introduced by partial esterification of the primary alcohol functions on the C6 carbon of the glucopyranosidic units with sulfate groups.³⁰ Centrifugation allowed us to separate three different aliquots, whose characterization data are reported in Table 1. The first one, termed “CNC4000”, was isolated as the supernatant suspension upon centrifugation at 4000 rpm; the remaining two, termed “CNC3000” and “CNC2000”, were separated from the residual material by performing centrifugation at 3000 and 2000 rpm, respectively. These aliquots (ESI,† Fig. S2) were composed of nanocellulose structures of different dimensions. According to the average hydrodynamic diameter determined by dynamic light scattering (DLS) in aqueous solution, CNC4000 was less polydisperse and it was composed of particles of diameters down to $82 \pm 15 \text{ nm}$; CNC3000 and CNC2000 displayed an average diameter as high as 310 ± 110 and $400 \pm 30 \text{ nm}$, respectively. Table 1 summarizes the properties of the three aliquots.

We measured the average molecular weights and polydispersities of each CNC aliquot by gel permeation chromatography (GPC) in chloroform against polystyrene standards. We converted CNCs and Avicel into their hexanoyl derivatives by reaction with the corresponding acyl chloride in pyridine at 80 °C, according to Scheme 1. Esterification destroyed the crystalline aggregation by suppression of the cooperative inter- and intra-chain H-bonds, yielding a triester cellulose polymer soluble in dichloromethane and chloroform. This material was suitable for conventional GPC analysis in organic solvents.

Table 1 Characterization data of cellulose nanocrystals (CNCs)

Aliquot	Centrifugation rate ^a [rpm]	DLS average diameter ^b [nm]	Average rod length (width) from AFM ^c [nm]	Aspect ratio from AFM	M _n ^d [Da]	M _w ^d [Da]	PDI ^d (M _w /M _n)	DP ^d
CNC4000	4000	82 ± 15	280 ± 70 (10 ± 2)	28	63 650	76 410	1.20	140
CNC3000	3000	310 ± 110	400 ± 60 (10 ± 2)	40	60 830	82 800	1.36	133
CNC2000	2000	400 ± 30	N/A	N/A	61 940	96 950	1.28	135
Avicel PH-101	—	45 ± 5 ^e μm			69 710	94 100	1.35	153

^a The centrifugation parameter defines the rate at which the nanocrystal fraction was isolated in the supernatant aqueous solution. ^b Estimated with the software LB-550. ^c Estimated from tapping AFM topographies acquired on nanocrystals deposited on glass from 0.01% w/w solutions. ^d Average molecular weights, polydispersity index (PDI) and degree of polymerization (DP = M_n/MW; with MW = 456 Da, molecular weight of the repetition unit of cellulose hexanoyl ester) were estimated from GPC measurements performed on the corresponding hexanoyl cellulose esters, synthesized according to Scheme 2. ^e Average dimension of Avicel was judged *via* optical microscopy (see the ESI for details).



Scheme 1 Full esterification of cellulose with hexanoyl chloride.

Ioelovich³¹ has shown that hydrolysis of Avicel produces nanocrystals with an average degree of polymerization (DP) of 120–140 and that, if the DP lowers at this average value, the crystallinity is lost. In our experiments, Avicel displayed a number average molecular weight M_n of 68 710 Da, while the CNC4000, CNC3000 and CNC2000 fractions showed a M_n value of 63 650, 60 830 and 61 940 Da with a DP of 153 for Avicel and of 140, 133, and 135 for CNC4000, CNC3000 and CNC2000 aliquots, respectively. The data confirmed that DP was not compromised by the hydrolysis reaction, even in the presence of a consistent decrease in the aggregate dimension of crystalline cellulose, and this could be taken as an indirect proof of preserved crystallinity. Looking at the weight average molecular weight M_w , Avicel displayed a M_w of 94 100 Da, while CNC4000, CNC3000 and CNC2000 fractions showed M_w of 76 410, 82 800 and 96 950 Da, respectively. The less monodisperse cellulose was CNC4000, with a polydispersity index (PDI) of 1.20. This was highly in accordance with the observed dispersity in the DLS hydrodynamic diameter, where an uncertainty of 11 nm was found over an average diameter of 82 nm. The other fractions were more polydisperse: CNC3000 showed a PDI of 1.36, reflecting the very high uncertainty on the hydrodynamic diameter, while CNC2000 and Avicel had a PDI of 1.28 and 1.35, respectively.

Atomic force microscopy (AFM) was useful for a first morphological characterization of the nanocelluloses: topographies were acquired on solution cast thin films of the three aliquots. The AFM topographies (see Fig. S3 and S4, ESI[†])

certified the presence of rod-like crystals. The dimensions of the rods were markedly different for each aliquot: the height distribution and the root mean square roughness increased in this fashion: CNC4000 < CNC3000 < CNC2000 (please refer to the ESI,[†] Fig. S4, for the histograms for each $10 \times 10 \mu\text{m}^2$ topography and Table S2 (ESI[†]) for the root mean square roughness values). These results clearly evidenced the increased dimension of nanocellulose rods in the CNC3000 and CNC2000 fractions. AFM allowed calculation of the average length and width of CNC4000 and CNC3000 fractions. The same could not be performed on CNC2000 due to the highest roughness of the sample (see Fig. S5, ESI,[†] for data for the sole CNC4000 fraction). According to AFM, CNC4000 was composed of rods with a length of 280 ± 70 nm, a width of 10 ± 2 nm and an aspect of ratio 28, while CNC3000 was composed of rods with a length of 400 ± 60 nm, a width of 10 ± 2 nm and an aspect ratio of 40. The width, calculated by difference in heights and hence very close to the real value, in each case suggested the presence of elementary nanofibrils that were cut by acid digestion at different lengths. CNC4000, which was revealed to be the less polydisperse aliquot according to DLS and GPC outcomes (with a PDI of 1.20), was deposited on silicon and further analyzed by the FE-SEM technique (Fig. 1), confirming the presence of rod-like nanocrystals and their dimensions, in agreement with AFM.

CNP deposition and hydrophobization

Cellulose nanopaper can be prepared from CNC suspensions in water by solution casting. As water evaporates, hydrogen bonds are established between nanocrystals, forming a network that detaches spontaneously as free-standing films. With the aim to produce the flattest nanopaper with limited voids, we cast CNC4000 solutions. We used as substrates Kapton foils, that present excellent flatness. 1 mg mL^{-1} of glycerol was added to the solution as a plasticizer. The free-standing films were transparent, flat and flexible (see Fig. S6, ESI[†]). The average thickness was $32 \mu\text{m}$.

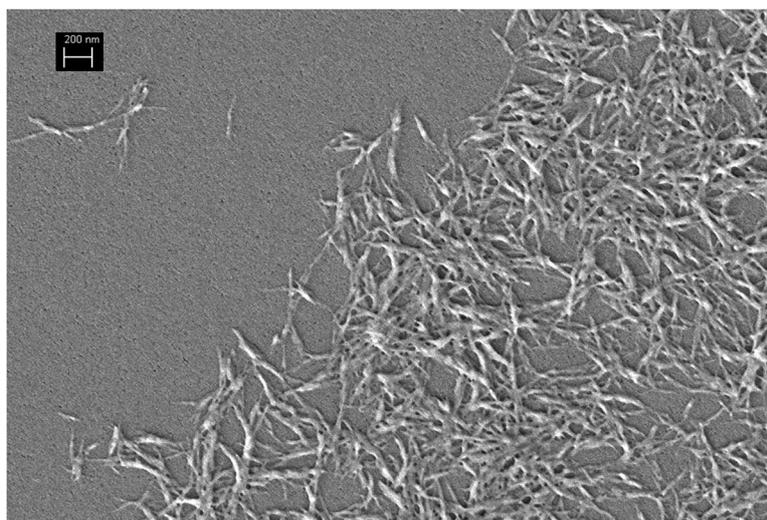
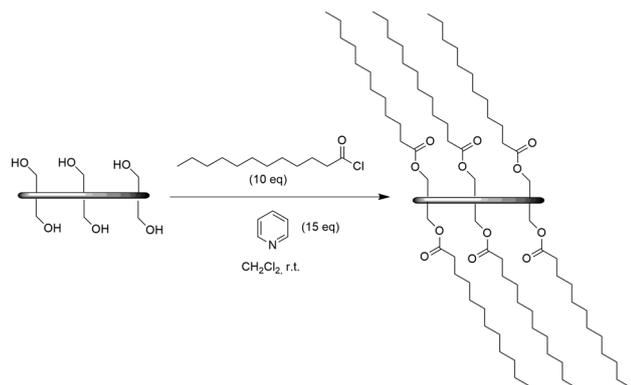


Fig. 1 FE-SEM micrograph of CNC4000 deposited by drop casting on silicon.



Scheme 2 Hydrophobization of nanopaper (CNP) with lauroyl chloride in dichloromethane and pyridine, producing C_{12} -CNP.

The surface functionalization was carried out by dipping the CNP thin film in a dichloromethane solution of lauroyl chloride and pyridine in a nitrogen filled glove-box at room temperature, according to Scheme 2. Pyridine played a role in the conversion of hydrochloric acid generated by the reaction in pyridinium chloride. The milder conditions of this reaction, with respect to the protocol presented in Scheme 1, allowed us to control the functionalization of nanopaper limiting the reaction to its surface. We attained nanopaper with the desired hydrophobicity by tuning the relative amounts of acyl chloride and pyridine used and reaction times, as discussed below. Four different reaction conditions were tested, as reported in Table S3 in the ESI.† At the end of each experiment, the success of the functionalization was detected by FT-IR analysis performed on the nanocellulose based films, recognizing the peak of the acyl C=O stretching at 1733 cm^{-1} . The use of high pyridine/cellulose molar ratios (entries 1 and 2) compromised the flexibility of nanopaper, resulting in brittle samples, even if shorter (1 h) reaction times were adopted. We attributed this to possible cellulose phase transitions similar to those caused by interaction with alkali.³² Consequently, we lowered the pyridine/cellulose molar ratios that did not compromise the nanopaper flexibility, while keeping the molar ratio between acyl chloride and cellulose higher than 5. We then chose the reaction conditions reported in entry 3 (the shortest reaction time with 10 equivalents of acyl chloride and 15 equivalents of pyridine). In order to demonstrate the correctness of our choice, we fixed the reaction conditions of entry 3 and carried out chemical modification experiments on CNP with lauroyl chloride changing the reaction time: we probed dipping times of 10, 30, 60 and 120 minutes. At the end of each experiment, we washed the samples with dichloromethane and ethanol and carried out elemental analyses to detect an approximate degree of substitution of cellulose (DS) depending on the reaction time.^{33,34} The results are collected in Table S4, reported in the ESI.† According to other authors, the degree of substitution (DS) of CNCs should be kept between 0.15 and 0.8 to ensure the involvement of only the skin of the nanocrystals and not the extension of the functionalization to their core.³⁵ We found that the DS value increased from 0.011 for 10 minutes reaction time,

to 0.023 for 30 minutes dipping and to 0.034 for 60 minutes dipping. The DS values were lower than the 0.15 limit value, but this is reasonable, because the functionalization involved only the surface of the nanopaper, while the elemental analyses are referred to the nanopaper bulk. Dipping CNP for 120 minutes yielded a DS of 0.018: the lower value could be reasonably ascribed to the loss of some material due to too long reaction times. A possible extension of the reaction to the core of nanocrystals and solubilization of the surface cellulose triesters formed in the reaction medium may be the origin of material loss during the washing process. In conclusion, we chose 1 hour as the total reaction time that, according to elemental analyses, yielded a DS of 0.034 without apparent loss of material.

Characterization of CNP and C_{12} -CNP

We decided to perform an extensive characterization of the hydrophobized nanopaper (C_{12} -CNP). Fig. 2a reports the FT-IR spectra that were acquired for CNP (black) and C_{12} -CNP (red). The hydrophobic CNP thin film spectrum did not show the

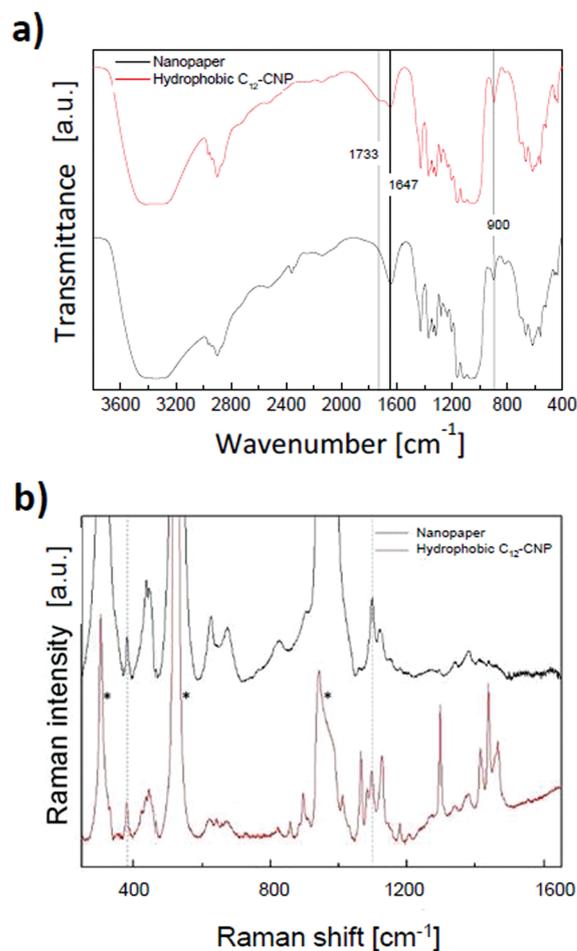


Fig. 2 (a) FT-IR spectra of nanopaper (black) and hydrophobic C_{12} -nanopaper (red) films. Vertical lines indicate signals centered at 1733 , 1647 and 900 cm^{-1} . (b) Raman spectra of nanopaper (black) and hydrophobic C_{12} -CNP (red) deposited on c-Si substrates. Dashed lines indicate, respectively, the cellulose Raman peaks at 380 cm^{-1} and 1096 cm^{-1} . Raman features related to silicon substrate modes have been labelled by *.

presence of adventitious pyridinium chloride salt formed during the reaction. The absence of adsorbed salt from the surface was confirmed by the absence of its characteristic and intense FT-IR bands at 2439, 1635, 1610, 1535, and 1485 cm^{-1} and by elemental analyses that revealed no increase in nitrogen content with the functionalization.³⁶ Moreover, the FT-IR spectrum of C₁₂-CNP showed the appearance of a distinct signal at 1733 cm^{-1} , which was ascribable to the C=O stretching of the ester group. The new band was partially overlapped with the band at 1647 cm^{-1} , attributed to crystallized water. The signal of free O–H single bond stretching, centred at 3400 cm^{-1} , was persistent, suggesting an incomplete functionalization of the cellulose backbone with ester groups. This supported the hypothesis that only the most reactive alcohol groups on the surface were transformed into lauroyl ester pendant groups by wet treatment. In a parallel work,^{35a} the reaction of CNCs suspended in DMF at 90 °C with acyl chlorides at different reaction times demonstrated progressive conversion of cellulose surface chains into a triester, with the reaction proceeding from the skin to the core of nanocrystals. This reactivity was hypothesized in our experiments too, and, in order to understand this aspect, a cautious consideration of nanopaper bulk and surface crystallinity changes was taken into account.

Both spectra presented a typical absorption profile found for samples mainly composed of cellulose I (the crystalline form mainly containing Avicel). As reported by Nelson and O'Connor earlier,³⁷ the intensity of the absorption band at *ca.* 900 cm^{-1} in the FT-IR spectrum increases with either a decrease in the crystallinity of the cellulose sample or a change in the crystal lattice from cellulose I to cellulose II or other allomorphs. Since our FT-IR spectra showed an increase in the mentioned band after hydrophobization, we carried out a deeper spectroscopic investigation on the effects of the dipping reaction to better understand the possible phase changes along with cellulose hydrophobization.

The Raman spectra of nanopaper (black) and hydrophobic C₁₂-CNP (red) are shown in Fig. 2b. The successful nanopaper functionalization was attested by the appearance of new Raman modes in the red spectrum. The Raman spectra of cellulose are very sensitive to the differences in conformation and structural order, which can affect the intensity, bandwidth and position of spectral features. In a comparative XRD/Raman investigation, Agarwal *et al.*³⁸ empirically demonstrated that the intensities of Raman peaks are differently affected by variations in the mass fraction of crystalline domains in cellulose materials. In particular, the relative intensity of the peak at 380 cm^{-1} , I_{380} , with respect to the peak at 1096 cm^{-1} , I_{1096} , was used in numerous cellulose studies as a measure of the degree of crystallinity.^{38–40} We measured an I_{380}/I_{1096} value of around 1.1 from the Raman spectra of Avicel PH-101 (Fig. S7, ESI†). This ratio decreased for the nanopaper Raman spectra (Fig. 2b). This agreed with the fairly lower polymerization degree found in CNC4000 with respect to Avicel. Conversely, the Raman spectra in Fig. 2b revealed a higher value of the I_{380}/I_{1096} ratio for the hydrophobic C₁₂-CNP, suggesting a structural reorganization of part of the cellulose containing the nanopaper after hydrophobization.

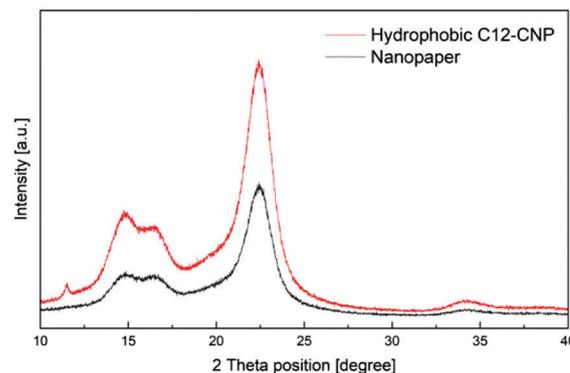


Fig. 3 XRD pattern of nanopaper before (black) and after (red) the hydrophobization process.

A deeper analysis of the cellulose structural changes was performed by X-ray diffraction measurements operating under glancing incidence conditions. This particular configuration enables the identification of phases with increased surface sensitivity, limiting the X-ray penetration depth to the near surface zone of the CNP samples. Before the hydrophobization treatment the XRD pattern of CNP, the black line in Fig. 3, showed the characteristic spectrum of the cellulose I/amorphous phase with diffraction peaks at 2θ angles of 14.7°, 16.4°, 22.4° and 34.4°, which could be assigned to (1–10), (110), (200) and (004), respectively.² Conversely, the spectrum of hydrophobic C₁₂-CNP (the red line in Fig. 3) was characterized by more intense and better resolved Bragg's diffraction peaks without any shift in the 2θ angle position. This suggested a lower amorphous character and a more ordered structure for C₁₂-CNP as a consequence of the reaction. Moreover, after surface functionalization, a low intensity diffraction peak at 11.5° appeared, which, coupled with an increase of the intensity in the range between 18° and 22°, could be ascribed to the presence of crystalline allomorphs of cellulose.² The line shape of the diffraction spectrum did not allow discrimination between the presence of a single and a mixture of allomorphs, and further analyses, beyond the scope of this paper, will have to be performed in the future to get a deeper understanding of these aspects.

Further investigation on the surface of CNP and C₁₂-CNP was performed by atomic force microscopy in tapping mode and by water contact angle measurements (see Table 2 and Fig. 4). Fig. 4 shows $2.5 \times 2.5 \mu\text{m}^2$ tapping mode AFM topographies of the pristine CNP surface with respect to the hydrophobic one. The former (Fig. 4a) showed the typical aggregation profile of CNC nanocrystals, with rods intimately connected to each other by their longitudinal dimension. The pristine CNP film

Table 2 Characterization data of cellulose nanopaper (CNP) and hydrophobic nanopaper (C₁₂-CNP)

	Water contact angle [°]	Root mean square roughness ^a [nm]
CNP	87 ± 4	7.7 ± 0.6
C ₁₂ -CNP	114 ± 6	5.0 ± 0.7

^a Measured using the software XEI.

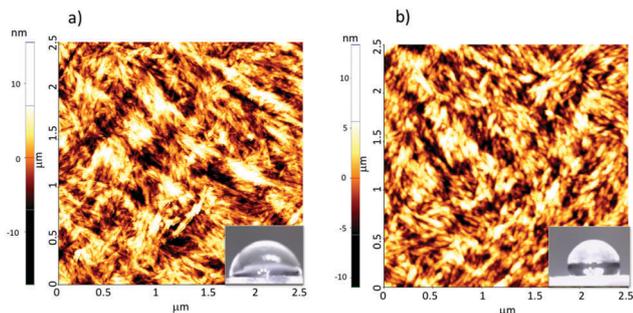


Fig. 4 Tapping-mode $2.5 \times 2.5 \mu\text{m}^2$ AFM topographies of (a) nanopaper from CNC4000 and (b) nanopaper after hydrophobization with lauroyl chloride. Insets: Water contact angle on the surface of the samples.

displayed a mean surface roughness of 7.7 ± 0.6 nm. The aggregation profile was still recognizable in the topography acquired after the functionalization based on lauroyl chloride and pyridine, which demonstrated how the film texture was preserved even though a surface reorganization had occurred. Upon turning the hydrophilic CNP thin film into a hydrophobic one, the root mean square roughness decreased down to 5.0 ± 0.7 nm. All these findings suggested surface functionalization and that lauroyl ester groups, possessing a linear and flexible aliphatic chain with a nominal length of approximately 1.6 nm, were homogeneously distributed over the surface of nanopaper, forming a layer potentially functioning as a barrier to water. This caused superficial fibres to swell, and the surface assumed a continuous film-like structure, with a corresponding decrease in roughness. FE-SEM micrographs of CNP and C_{12} -CNP, reported in Fig. 5, were consistent with the picture given by AFM. The apparent increased compactness and a more agglomerated structure observed in the micrograph recorded for C_{12} -CNP with respect to the hydrophilic CNP agreed with the decrease in surface roughness detected by AFM (compare also Fig. S8, ESI† with SEM micrographs acquired for larger areas).

Further information was offered by water contact angle measurements. In the case of bare CNP thin films, the water contact angle was equal to $87 \pm 4^\circ$ (Table 2), but only for the

first few seconds, since the water drop penetrated progressively into the nanocellulose film. This demonstrated the easy uptake of water into the pristine CNP thin films, whose primary effect is swelling and overall weakening of the film compactness. As mentioned in the introduction, this CNP limitation is still an open challenge in this field. A similar behaviour was observed for CNPs subjected to functionalization for 10, 30 and 40 minutes. Conversely, the contact angle of distilled water on the surface of the hydrophobic C_{12} -CNP thin film was equal to $114 \pm 6^\circ$, which proved to be a dramatic change in the grade of wettability due to the successful functionalization. A further proof along this direction was the stability of the water drop onto the hydrophobic CNP. This allowed us to wash the C_{12} -CNP in ethanol and water at the end of the hydrophobization reaction.

Water permeability tests

The promising properties of C_{12} -CNP prompted us to investigate the water intake of these CNP-based thin films by means of electrochemical impedance spectroscopy (EIS). So far, the dramatic change in the surface tension of the C_{12} -CNP thin film, recorded by contact angle measurement, neither furnished enough information about the water intake in the nanopaper bulk, nor allowed us to give a quantitative interpretation of the apparently increased surface hydrophobicity. For this purpose, we performed electrochemical measurements, which could provide a clear view about the water intake into our CNP samples with time and effectively prove the increased stability gained by C_{12} -CNP in water. EIS was previously successful in the investigation of protective coatings against metal corrosion^{41–43} and biodegradation of enteric coatings.⁴⁴ In corrosion studies, by performing impedance measurements at low and high frequencies on metals covered with polymer protective coatings, it was possible to calculate their porosity.⁴⁵ The porosity was an expression of the number of defects per unit area: a defect-less metal protective coating would not be permeable to ions, oxygen and water. Conversely, defects would determine progressive penetration of the aqueous solution through the coating to the underlying

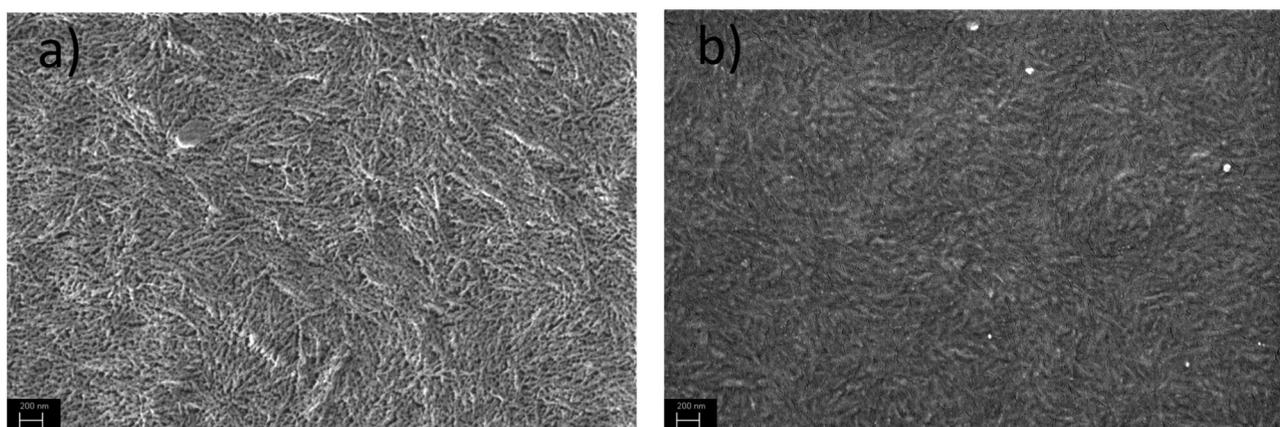


Fig. 5 FE-SEM surface micrographs of (a) CNP and (b) C_{12} -CNP (scale bar 200 nm).

metal. The presence (or absence) of thin channels of electrolyte running across the coating would appear as a coating bulk resistance R_b . A second parameter, the wetted area, was related to the fraction of the metal surface wetted by the aqueous solution. It could assume a different value from porosity when the aqueous solution contacting the electrode from a thin pore was spread rapidly between the coating and the metal.

Accordingly, CNP and C_{12} -CNP thin films were placed onto a polycrystalline Au electrode to carry out impedance spectroscopy, by applying a sinusoidal potential with a small amplitude (*i.e.* 10 mV) to the electrode. Different from those well-established corrosion tests, we performed measurements in a fully capacitive mode, namely avoiding any faradaic reactions (*i.e.* the set potential fixed at 0 V; for further details on the experimental setup see the ESI,† Fig. S9). The dramatic difference between CNP and C_{12} -CNP was expressed here by the necessity to fit the impedance data with two different equivalent circuits, termed circuit 1 for CNP and circuit 2 for C_{12} -CNP (reported in Fig. 6a and b, respectively). The two circuits presented the following electrochemical components: the resistance of the electrolyte solution (R_s), the above described resistance of the film bulk (R_b), the capacitance of the film bulk (C_b), a constant phase element that described the electrical double layer at the interface between the Au electrode and the CNP sample (CPE_1), and a constant phase element that described an additional capacitive barrier detected solely in the C_{12} -CNP film (CPE_2).

The open porosity P was calculated from the R_{bt}/R_b ratio, in which R_{bt} is the theoretical resistance of a layer of pure electrolyte featuring the same thickness as CNP, while R_b was the nanopaper bulk resistance. As shown in the plot presented in Fig. 6c, over time the evolution of the dimensionless P parameters for pristine- (black squares) and C_{12} -CNP (red circles) showed a difference of almost two orders of magnitude in the porosity value between the two different nanopaper samples recorded in more than two hours. Although the porosity of C_{12} -CNP was much lower than that of CNP, it was higher than that found for the most insulating coatings:^{45,46} dried and

perfectly insulating coatings showed P values of around 10^{-9} to 10^{-8} , whereas partially wetted and/or degraded ones yielded higher P values, up to 10^{-4} , closer to the values found here for C_{12} -CNP. We attributed this behaviour to the presence of crystallization water in our nanopaper ($\sim 8\%$ by weight, see the ESI,† Table S4, for details), which was not removed by the treatments performed. However, the transition from 10^{-4} porosity for C_{12} -CNP to 10^{-2} for CNP resulted in the preservation of the former and complete dissolution of the latter in water. The kinetics of the dissolution process of CNP in water was detected by monitoring the admittance value of CPE_1 as a function of time. The corresponding plot, shown in Fig. 6d, provided a time constant equal to 14 minutes. This kinetics was representative for those samples that did not degrade almost instantaneously upon immersion in water. In circuit 2, the presence of two in-parallel branches connecting R_b or C_b intrinsically certified no significant uptake of water, and the in-series CPE_2 could be directly correlated with the hydrophobic pendant groups on the nanopaper. The capacitive barrier value was $54(\pm 12) \mu\text{F cm}^{-2}$; in this case, as well, the difference from ideal capacitance values reported elsewhere for dry coatings was attributed to the crystallization water content of nanopaper.

Experimental

Materials and methods

All reagents were purchased with the highest commercial quality and used without further purification. Avicel PH-101 was used as the starting material for nanocrystalline cellulose isolation. Dry dichloromethane and pyridine were stored and dispensed in a nitrogen filled glove-box. Esterification reactions on nanocellulose were carried out under a nitrogen atmosphere in oven-dried glassware, using dry solvents. Sonication of water suspensions was carried out with a Branson Sonifier 250. FTIR spectra were recorded on a Perkin-Elmer Spectrum BX spectrophotometer using dry KBr pellets when stated. Dynamic light scattering was carried out on a Particle Size Analyzer Horiba LB-550. A micrometer was used to determine the nanopaper thickness. Contact angle measurements were conducted using bi-distilled water. CHEM 3D Pro v. 12.0 drawing software was used to calculate the theoretical length of the dodecanoyl group in the *in vacuo* optimized geometry.

Hydrolysis of cellulose and nanocrystal isolation

40 mL of deionized water were introduced in a 250 mL three necked round-bottom flask equipped with a water condenser and a mechanical stirrer. Then, the flask was cooled in an ice bath and 40 mL of concentrated H_2SO_4 were added. After that, 4 g of Avicel PH-101 were added and the suspension was warmed to 50°C for 80 minutes. The system was cooled to room temperature and the mixture was transferred to polypropylene centrifugation tubes. Centrifugation at 4000 rpm was repeated replacing the supernatant solution with fresh deionized water until the pH was approximately 1. Then the precipitate was suspended in deionized water with the aid of a

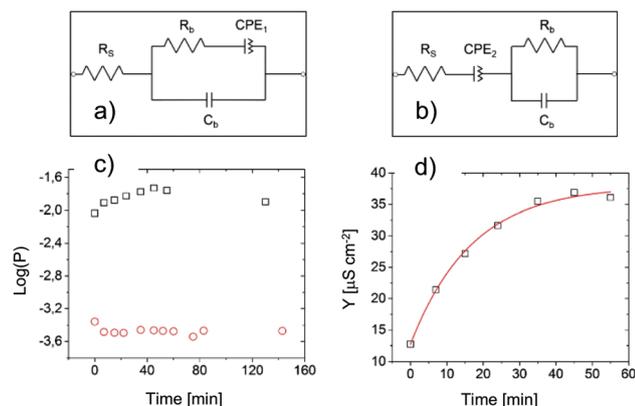


Fig. 6 (a) Equivalent circuit 1 (CNP) and (b) circuit 2 (C_{12} -CNP); (c) logarithm of the open porosity vs. time plot. Black open squares and red open circles stand for the hydrophilic and hydrophobic CNP films, respectively; (d) admittance Y vs. time plot. The red line is the exponential fit.

tip sonicator (power 2, duty cycle 60%, time 10 min) and dialyzed against distilled water until neutrality using a cellulose nitrate membrane with a molecular weight cut-off of 12 400 Da. The resulting suspension was transferred to polypropylene centrifugation tubes for the final fractionation as described in the ESI† and the Results and discussion paragraph.

Esterification of nanocrystalline cellulose with hexanoyl chloride

4 mL of nanocrystal solution were transferred to a 25 mL two necked round bottom flask. Water was distilled through a rotary evaporator, leaving a nanocellulose transparent film residue that was dried under vacuum. Then, the nanocellulose was weighed, and the flask was conditioned with nitrogen. 3 mL of dry pyridine were added, followed by esanoyl chloride (6 equivalents with respect to the amount of nanocellulose). The reaction mixture was heated at 80 °C for one night. The mixture turned from colourless to brown and the nanopaper film was completely consumed. The reaction mixture was cooled to room temperature and poured in a beaker containing 20 mL of HCl 3 M and some ice. Then it was transferred to a 100 mL extracting funnel and extracted with dichloromethane (3 × 20 mL). The organic extracts were collected and washed with a 20 mL of a saturated solution of NaHCO₃ and a saturated solution of NaCl (2 × 20 mL). After that the organic extracts were dried over Na₂SO₄ and filtered and the solvent was removed under reduced pressure. A brown solid was isolated. The crude material was purified by recrystallization from dichloromethane–methanol. A yellowish rubbery solid was isolated. FT-IR (KBr): ν 2960, 2855, 2360, 1740, 1460, 1261, 1162, 1055, 806 cm⁻¹.

GPC molecular weights and polymerization degree determination

GPC analysis was carried out at room temperature using a Malvern Viscotek TDA 305 equipped with a Tosoh Bioscience TSKgel G3000HHR column (7.8 mm i.d. × 30.0 cm *l*) using a refractive-index detector with chloroform as solvent. Calibration was performed using polystyrene standards. The polymers were dissolved in chloroform at 1 mg mL⁻¹ concentration and filtered prior to the measurement with 0.22 μ m PTFE filters.

Nanopaper preparation

1 mg mL⁻¹ of glycerol was added to a 1.8% w/w water suspension of cellulose nanocrystals. The suspension was sonicated for 20 minutes and it was poured on a Kapton foil and left to evaporate at 40 °C in a common laboratory oven. At the end of the evaporation the nanopaper thin films detach spontaneously from the substrate. A nanopaper with an average thickness of 32 μ m and an area of approximately 5 × 5 cm² was obtained. For the following experiments the nanopaper was cut into 2 × 2 cm² or 1 × 1 cm² samples.

Hydrophobization reaction on nanopaper

The reaction was carried out in a nitrogen filled glove-box. A glass vessel was filled with 100 mL of anhydrous dichloromethane, 3.4 mL (42 mmol) of anhydrous pyridine and 6.5 mL

(28 mmol) of lauroyl chloride. Then, a 455 mg sheet of nanopaper (2.8 mmol) was dipped in the mixture at room temperature for 1 hour. The reaction mixture turned from colorless to yellow. The nanopaper was removed, washed with 20 mL (4 × 5 mL) of clean dichloromethane, 20 mL of absolute ethanol and 20 mL of distilled water, and dried under vacuum. Finally, it was characterized by FT-IR spectroscopy, AFM, and contact angle measurement.

Elemental analyses

Elemental analyses were performed on a Carlo Erba EA 1108 CHNS Elemental analyzer. Sample preparation: the same nanopaper sample (prepared without a glycerol additive) was cut into different pieces. Each sample was functionalized with pending lauroyl groups by dipping under the same conditions described above for (i) 10 minutes, (ii) 30 minutes, (iii) 60 minutes and (iv) 120 minutes. At the end of the experiments the samples were washed with dichloromethane and ethanol and dried under vacuum.

Raman spectroscopy

The Raman spectra of nanopaper were collected using a LabRAM HR Horiba-Jobin Yvon spectrometer with a 784 nm excitation laser source. The nanopaper samples were deposited on silicon by drop casting. The measurements were carried out under ambient conditions at a low laser power (1 mW) to avoid laser induced damage. The Raman band recorded for a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be around 1 cm⁻¹.

Atomic force microscopy

Atomic force microscopy topographies were taken using a Park XE-100 SPM system microscope. Images were acquired in the tapping mode using tips (Type PPP-NCHR) on a cantilever of 125 μ m length, about 330 kHz resonance frequency, 42 N m⁻¹ nominal force constant and <10 nm guaranteed tip curvature radius. Surface areas were sampled with a scan rate of 1 Hz. The topographies were analysed using the software XEI (Park System Corporation, version 1.8.0).

FE-SEM images

The morphology of the surface of nanocrystalline cellulose was analyzed by FE-SEM, on a Field Emission Scanning Electron Microscope ZEISS Meriln[®] equipped with a GEMINI II[®] column and Beam-Booster, with acceleration voltages between 0.05 and 30 kV and 0.8 nm as the best resolution, four optional detectors for SE and BSE, charge compensation and an *in situ* sample cleaning system. 1 × 1 cm² quartz glasses or silicon slabs with 1 × 1 cm² area were used as substrates for FE-SEM measurements. All samples were allowed to dry overnight before analysis. For CNC4000 investigation, a solution 0.01% by weight of nanocrystals in water was drop cast on a silicon slab and after two minutes the solution residue was removed with filter paper. For nanopaper investigation, the pristine solution of CNC4000 was drop cast on quartz. One replicate was subjected to the hydrophobization reaction as described above.

X-Ray diffraction measurements

X-ray spectra of the cellulose nanopapers were obtained before and after hydrophobization treatment using a PANalytical EMPYREAN X-ray diffractometer operating in the parallel beam geometry under glancing incidence conditions. The diffractometer was equipped with a copper radiation source (CuK α -radiation $\lambda = 0.154186$ nm operating at 40 kV/40 mA), X-ray mirror and post-sample collimator coupled with a flat graphite monochromator to ensure an intense monochromatic quasi-parallel incident beam for a good signal to noise ratio and an improved resolution. The data were recorded on samples of nanopaper of the same batch and thickness maintaining the incident angle ω (the angle between the incident beam and the sample surface) fixed at 1.0° and collecting the signal for 15 s per step with a 0.02° step size in the range between 10° and 40°.

Electrochemical impedance spectroscopy characterization

The impedance measurements were carried out in the following electrolytic solution: 0.1 M NaCl and 10 mM phosphate buffer set at pH 7.4. A home-built stage was used in order to guarantee a stable electrical connection between the working electrode (*i.e.* Au-coated quartz slide) and the counter electrode, which is a Pt wire (\varnothing 1 mm). The NCP thin film was placed onto the gold-coated quartz slide. A further home-made system was built up for confining the electrolytic solution as well as to fix the area wetted by the aqueous solution (*i.e.* 0.59 cm²). The impedance measurements were performed using μ -AUTOLAB type III equipped with NOVA 1.10 software. The set potential was fixed at 0 V with an amplitude oscillation of 10 mV. The frequency range spanned from 10⁵ Hz to 10⁻¹ Hz with an acquisition time equal to 5 s. The electrochemical fits were performed by using the NOVA 1.10 software. According to our experimental setup, the R_{bt} is equal to 0.42 Ω . As well-defined in ref. 45, R_{bt} is the theoretical resistance of a layer of electrolyte that occupies the same volume of our thin film during the electrochemical measurements.

Conclusions

Performing acid hydrolysis of Avicel we were able to isolate water suspensions of a cellulose nanocrystalline material in good yields. The nanocrystals were morphologically characterized by AFM and FE-SEM microscopies. The molecular weight of the cellulose polymer corresponding to the distinct crystalline structure was detected by gel permeation chromatography against polystyrene standards of the corresponding hexanoyl triesters, finding polymerization degree (DP) values close to that of the starting microcrystalline material.

The nanocrystals with the lowest dimension, but a high aspect-ratio and low polydispersity, were used to prepare free-standing cellulose nanopaper (CNP) thin films. The cellulose nanopaper was hydrophobized by dipping in a dichloromethane solution of lauroyl chloride and pyridine and the preserved crystallinity, morphology and improved stability to water were demonstrated by AFM and FE-SEM microscopies,

contact angle measurements, XRD spectroscopy and electrochemical water uptake experiments.

The hydrophobized nanopaper demonstrated in the present study displayed a very low degree of substitution, compatible with functionalization limited only to its surface. The treatment had an important impact on the water resistance properties of the nanopaper: the lauroyl functionalization layer yielded a nanopaper with significantly decreased porosity, as judged from electrochemical impedance spectroscopy. The electrochemical study highlighted the macroscopic bulk differences between the pristine CNP and the C₁₂-CNP films in terms of open porosity. The former was quickly degraded upon water exposure due to a fast water sorption. The latter was perfectly stable in water throughout the experiment timescale. This supported our claim that the stability of nanopaper in water had been significantly improved. We can conclude that C₁₂-CNP represents a very promising substrate for biodegradable and printed electronic devices and sensors.

Conflicts of interest

There are no conflicts to declare.

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