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Cellulose nanofibril core-shell silica coatings and their conversion into thermally stable nanotube aerogels

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A facile water-based one-pot reaction protocol for obtaining 20 nm thick uniform silica coatings on cellulose nanofibrils (CNFs) are herein presented for the first time. The fully covering silica shells result in a thermal stability of the CNFs improved by ca. 70 °C and 50 °C under nitrogen and oxygen atmosphere, respectively. Heating of the core-shell hybrid fibres to 400 °C results in complete degradation/removal of the CNF cores, and demonstrates an inexpensive route to large-scale preparation of silica nanotubes with the CNFs used as templates. The key to a uniform condensation of the silica (from tetraethyl orthosilicate) to the cellulose is a reaction medium that permits in-situ nucleation and growth of the silica phase on the fibrils, while simultaneously matching the quantity of the condensed silica with specific surface area of the CNFs. Most coatings were applied to bundles of 2–3 associated CNFs, which could be discerned from their negative imprint that remained inside the silica nanotubes. Finally, it is demonstrated how the coated nanofibrils can be freeze-dried into highly porous associated silica/cellulose aerogels with a density of 0.005 g/cm³ and how these hybrid aerogels preserve their shape when extensively exposed to 400 °C under air (>6 h). The resulting material is the first reported silica nanotube aerogel obtained by using cellulose nanofibrils as templates.

1. Introduction

Thermally resistant cellulose nanofibrils (CNFs) are of interest in many envisioned applications where the cellulose “building block” may be exposed to temperatures different from its natural environments. From an engineering perspective, thermally stable CNFs could be used as filler for reinforcement in polymers processed at higher temperatures, but also in the development of porous and more heat resistant bio-based insulation materials^{1–6}. Other applications may include such CNFs as gas and liquid barrier agents in packing materials, or as a paper additives^{1–6}. However, the cellulose structure decompose into carbon residues by oxidation of the $\beta(1\rightarrow4)$ -glycosidic ether bonds in the cellulose backbone (depolymerisation, reduction of DP) at ca. 220 °C, followed by decomposition of the cyclic carbon glucose residues into char and gas (>300 °C)^{7–10}. This degradation is catalytically enhanced (resulting in premature degradation) by sulphite groups remaining on the surface of the CNFs from the sulphuric acid extraction used to isolate the fibrils from their natural habitat, or the presence of metal/metal oxide nanoparticles, e.g. silver, gold, platinum and titanium, zirconium and aluminium^{11–15}.

In the past, flame retardant finishes containing nitrogen and phosphorus compounds have been reported for cotton cellulosic fabrics^{16–18}. These coatings provide a temporarily reduced susceptibility of the cellulose to undergo thermal degradation but are inevitably limited by their quantities and consumption rates^{19, 20}. The use of alternative acids during the CNF extraction procedure provides a first step to prevent the thermal degradation of the CNFs, e.g. hydrochloric/phosphoric acid²¹. Espinosa et al. recently compared phosphoric with sulphuric acid and showed that phosphoric acid induce substantially smaller catalytic action during the degradation of CNFs at elevated temperatures²². However, the influence of the different acid remains on the degradation mechanisms are unclear in terms of initiation, oxidation and/or influence of mechanistic degradation patterns (char formation), and in many cases the thermal stability of the raw (untreated) cellulose material prevails over the extracted CNF material^{23–26}.

Temperature-resistant coatings that improve the thermal performance of virgin cellulose nanofibrils have received significantly less attention than the selection of acid used for the isolation of the CNFs. Generic CNF surface coating-modification methods to increase the onset temperature of cellulose degradation are therefore missing. To some extent this can be related to the extraction and processing of cellulose nanofibrils with characteristics affected by the adopted

conditions and possible impurities, but also due to the fact that cellulose nanofibrils disclose different properties depending on the origin of the CNF crystals. Some of these differences in CNF characteristics were recently described by Sacui et al. in terms of size, morphology, crystallinity, surface energy, and chemical character.²⁷ This inevitably affects the possibilities to develop generic methods for improved thermal performance of the CNFs, e.g. since most surface modifications ultimately rely on predictable surfaces to be modified.

In this article, we demonstrate how it is possible to improve the thermal performance of CNFs extracted from bacterial cellulose by encapsulating the individual fibrils in uniform layers of silica. The necessary reaction conditions for preparing these silica-cellulose hybrid fibres are for the first time presented, opening for large-scale preparation of more heat resistant “core-shell” cellulose/silica hybrid nanofibrils. The thermal performance was improved by ca. 70 °C in nitrogen and 50 °C in oxygen. The silica-coated CNFs were further heated to >400 °C to remove the cellulose cores, which resulted in silica nanotubes with internal dimensions equivalent to the dimensions of the original cellulose nanofibrils. Previously, silica nanotubes have received attention as prepared by deposition on porous aluminium oxide substrates²⁸, coating of carbon nanotubes²⁹, organic molecular deposition (including surfactants³⁰, acids³¹, block copolymers³² and gels^{33, 34}), or coating and etching of TiO₂/CTAB pre-treated cotton fibers³⁵ as templates.³⁶ It is herein demonstrated that cellulose may present a viable alternative for large-scale and more economical preparation of several micrometre long silica nanotubes via the presented templating reactions. The coated CNFs were also freeze-dried into porous cellulose/silica aerogels that were heated 400 °C for 6 hours under air, thereby demonstrating a method to transform the “core-shell” nanofibers to the first reported silica nanotube aerogels.

2. Experimental section

2.1 Preparation of cellulose mats from bacteria cultures

Bacterial cellulose was grown from a 20 litre sterilized glucose solution inoculated with *Acetobacter Xylinus* – ATCC 23767^{27, 37}. The solution composition was per litre: 20 g of d-glucose (Dextrose, ACS reagent, Sigma Aldrich), 5 g of yeast extract (Fluka, CAS 8013-01-2), 1.15 g of anhydrous citric acid (reagent grade, Scharlau), 5.7 g of magnesium sulphate (puriss, p.a., Fluka), and 12.25 g of triphosphate water from Scharlau (5.0 g of peptone, 2.5 g of sodium chloride, 4.5 g of disodium phosphate, and 0.75 g of potassium phosphate), and 1 vol.% ethanol (96%). The 20 L solution was inoculated with a 150 mL pre-inoculated and fully developed bacteria culture that had been scaled from a 5 mL sample prepared from the preserved strain in the glass ampoule. The time required to generate the fully developed bacteria culture and uniformly growing cellulose pellicle mats in each pre-inoculated sample was 48 h at 28 °C. The weight of the wet microbial cellulose pellicle mat formed on the surface of the up-scaled growth medium was ca. 1.0 kg (including the growth medium inside the mat) after 48

hours. The mats were cut into 1 cm³ cubes that were brought to boiling repeatedly in distilled water (5x) until no residual growth medium could be detected. The pieces were then boiled 2 times in 10 vol.% concentrated NaOH (2 L x 2) for 20 min, with intermediate rinsing with distilled water until neutral pH≈7.

2.2 Extraction of cellulose nanofibrils by acid hydrolysis

Prior to the extraction of the CNFs, the 1.0 kg of bacterial cellulose cubes was shredded in a regular kitchen blender and compressed in a SEFAR polyamide mesh (PA 1000 120/305–35W with 46 µm openings) to remove most of the water. This was performed to facilitate spreading/distribution and acid diffusion into the cellulose material during the early stages of the hydrolysis reaction, i.e. for a more even degradation of the amorphous parts. The total mass of wet cellulose was 148 g. The water remaining in the compressed cellulose was 87.2 ± 0.8 % (evaluated from 3 samples), corresponding to dry bacterial cellulose content of 18.9 g. Fig. S1 shows the bacterial cellulose during removal of growth medium (a) and the shredded material before exposure to acid (b).

The 148 grams of wet cellulose was added to a 2 L aqueous hydrochloric acid solution containing 30 vol.% of reagent grade acid (Merck KGaA), and stirred at 60 ± 0.5 °C (300 rpm). The suspension was stirred for 9 hours until no visible traces of cellulose pieces were apparent and the solution had acquired an even beige colour. The extraction was terminated by addition of 2 L cold MilliQ water and isothermally centrifuged at 10 000 rpm (15 °C) for 10 min, four times. Between the centrifugation cycles, the cellulose was collected at the bottom of the centrifuge tubes; the acidic supernatant was decanted and replaced with fresh Milli-Q water (50 °C), followed by re-dispersed using a high-shear mixer (Ultra Turrax DI-25) for 5 min. After the third cycle, a neutral pH was obtained and the supernatant was transparent. By the last addition of MilliQ water, this sample was adjusted to 0.4 wt.% solid content in the pure water. The total amount of extracted CNFs from the entire 1 kg mat (or 18.9 g of corresponding dry bacterial cellulose) was dry 10.4 grams (55 wt.% yield). For all subsequent experiments, this cellulose was used containing 4 mg of pure CNFs per mL. The specific surface area of the CNFs was calculated to ca. 159 m² per gram from size distributions obtained by manual counting of min 500 fibrils deposited on TEM grids, which is in agreement with the calculated value of 189 m²/g by Roman et al.¹⁴ and lower experimental value of 103 m²/g for dry bacterial cellulose fibrils by Olsson et al.³⁸.

2.3 Silica coating cellulose nanofibrils

Tetraethyl orthosilicate (TEOS, ≥98%) and ammonium hydroxide (aq. 28 wt.%) were purchased from Sigma-Aldrich. Methanol, ethanol and 2-propanol were obtained from VWR (reagent grade, ≥99.8 %). High-resistivity MilliQ water (“Type 1”, following ISO 3696 and ASTM D1193–91, defined as 18.2 MOhm.cm at 25 °C) was used in all the sample preparation procedure. Methanol, ethanol or 2-propanol in water was used due to the different abilities of these alcohols to slow down the

silica precursor condensation reaction³⁹. The evaluated reaction media were methanol, ethanol or 2-propanol, which contained 18 vol.% water. Ammonia was used due to its previously reported ability to catalyse the Stöber reaction⁴⁰. In all reactions, the final addition of Tetraethyl orthosilicate (TEOS) was carried out as concentrated directly to the reaction to allow the TEOS to hydrolyse and initiate its condensation in-situ onto the CNFs, i.e. to avoid premature self-nucleation of the silica precursor into solitary silica particles⁴⁰.

2.4 Determination of cellulose to TEOS ratio and effect of alcohols on condensation chemistry

A sample of 0.67 mL (2.7 mg CNFs) or 2.0 mL (8 mg CNFs) from the extracted suspension was centrifuged, decanted from water and re-dispersed via 3 times solvent exchange into 2.55 mL mixture of 82 vol.% alcohol (methanol, ethanol or 2-propanol) and MilliQ water in a 50 mL polypropylene tube. The CNF suspension was then ultrasonicated in an ultrasonic bath for 5 min at an average intensity of 300 W. The polypropylene tube (reactor) was then mounted onto a vortex shaker (Vortex Genie 1, US) and 0.057 mL aqueous ammonia solution was injected into the reactor. Finally, the coating condensation reaction was initiated by adding 0.06 mL tetraethyl orthosilicate (TEOS). The amount of TEOS used was calculated to yield a complete coverage of fully condensed silica on the CNFs, and the ratio of aqueous ammonia to TEOS was kept constant for all reactions. The reaction proceeded at 20 °C (under maximum shaking) for 3 h to reach complete condensation of the silica phase. The resulting core-shell CNFs were centrifuged 90 seconds at 1000 RCF in a tabletop Eppendorf Minispin centrifuge and washed three times with ethanol. The most favourable reaction medium was established by using 0.67 mL of the extracted CNF suspension (2.7 mg). After mixing all components, the masses of cellulose in the reaction tube were 1 mg/mL or 3 mg/mL. All samples are referred to as the mass of fibrils modified in the reaction tube per volume of reaction suspension.

2.5 CNF aerogel preparation

The reaction conditions allowing for complete coverage of the CNFs (above 1 mg/mL) was up-scaled 50 times to prepare sufficient material for aerogel preparation (with the only difference of using mechanical stirring at 300 rpm). The neat CNF and the coated CNF suspensions were both adjusted to a

solid content of 5 mg/mL (resulting in final density of 0.005 g/cm³ for the aerogels). The suspensions were subsequently poured into cubic-shaped silicone moulds, which were frozen from the bottom up using liquid nitrogen (only the bottom surface of the mould were in contact with the liquid nitrogen). The moulds were then transferred into a commercial freeze drier (Scanvac Coolsafe) and dried over the period of 3 days (in order to ensure complete evaporation of water inside the nano-sized network).

2.6 Silica nanotube aerogel preparation

The prepared CNF–SiO₂ aerogels were converted into silica nanotube aerogels *via* thermal treatment at 400 °C for 6 h in air. Shorter times (ca. 1 h) resulted in only a partial conversion of the material due to the good thermal insulation of the aerogels. The conversion and the stability of the final silica nanotube aerogel were demonstrated by placing a cubic CNF–SiO₂ aerogel side-by-side with a cube of neat CNF aerogel in a thermal gradient (200–400 °C, top-bottom surface). The cross-sections of the samples were photographed through a transparent window of borosilicate glass every 4 s for 1 h (time-lapse video available in supplementary info).

2.7 Characterization

Transmission electron micrographs were obtained using a Hitachi HT7700 microscope operated at 100 kV. Samples of particles were deposited onto holey carbon-coated 400 mesh copper grids (TED PELLA, USA) from ultrasonicated suspensions of particles in ethanol. Scanning electron microscopy was performed on a Hitachi S-4800, after Pt/Pd sputtering. A Mettler-Toledo SDTA/TGA905 thermo-balance was used to obtain the mass loss of the nanoparticle samples before and after the surface modification. Prior to the measurements, the samples were heated at 140 °C for 20 min to eliminate adsorbed water on the CNFs surface. In the TG experiments the samples were heated from 100 to 800 °C at a heating rate of 10 °C/min in 70 µL alumina crucibles under both nitrogen and oxygen atmosphere. X-ray diffraction (XRD) measurements were conducted on the compressed aerogel cubes (resulting in thin square-shaped films) in a PANalytical X'Pert Pro diffractometer (Almelo, The Netherlands) fitted with an Empyrean Cu–K α tube (45 kV, 45 mA) and a 1D X'Celerator detector with a 1.00 arcmin step size.

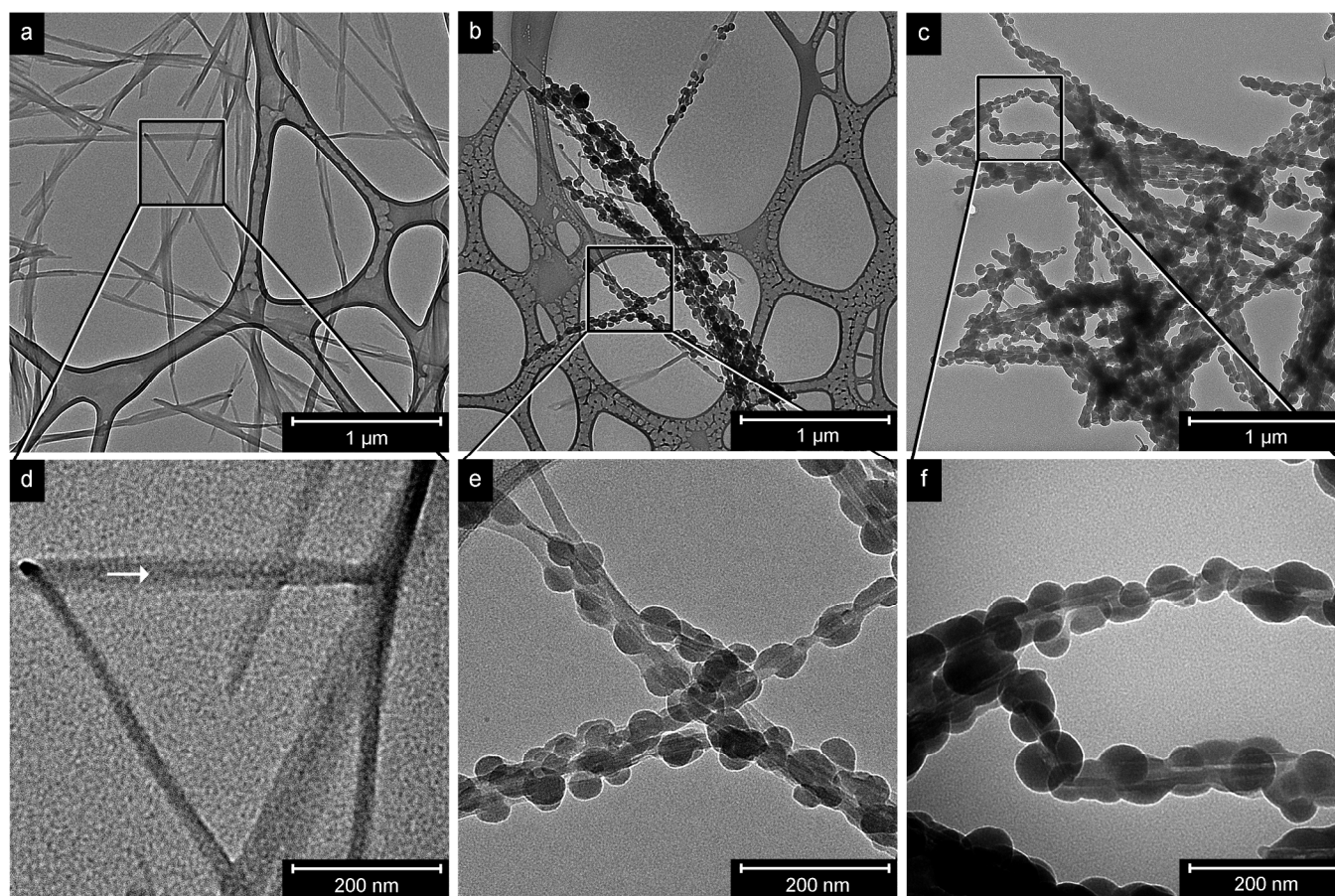


Fig. 1. Transmission electron micrographs of uncoated cellulose nanofibrils with surface area of ca. $160 \text{ m}^2/\text{g}$ and an average overall length of 2–3 μm (a), and silica embedded CNFs coated in 2-propanol at different CNF concentrations: 3 mg/mL (b) and 1 mg/mL (c). Fig. 2 (d), (e) and (f) highlight areas in (a), (b) and (c), respectively. The uncoated and coated CNFs were deposited as separate from an ethanol solution, and associated together during evaporation of the ethanol.

3. Results and discussion

3.1 Morphology of silica coated CNFs

Figure 1 shows that preparation of completely coated nanofibrils relied on finding a concentration of the uncoated CNFs in suspension (Fig. 1a) that matched with the number of SiO_2 nuclei formed and full amount of silica condensed to the surface area of the CNFs. The 0.27×10^{-3} moles of condensed TEOS precursor (0.06 mL) were unable to cover the 1.27 m^2 CNF surface area when 8 mg (3 mg/mL) of CNFs was used from the suspension of extracted CNFs, Fig. 1b and e. Complete coverage was only reached when the amount of extracted CNFs had been reduced to 2.7 mg and the targeted CNF surface area was decreased to 0.43 m^2 , as shown in Fig 1c and f. At this point, the effective amount of TEOS per mg of CNFs was 0.1 moles per g of CNFs. The silica shell on the fibres had an average thickness of ca. 20 nm (measurements of ca. 40 particles), where the thinnest coated sections were ca. 15 nm and the thickest 45 nm. The thicker sections corresponded to regions where the silica had grown as nucleated half-spheres on earlier formed silica (Fig. 1f). The cause for this formation of the uneven necklace-like morphology stemmed from a heterogeneous and time-differentiated nucleation along the

fibrils on the most favourable/accessible spots on the CNFs. Figs. 1d to f show greater magnifications on selected areas of the micrographs on the top. In Fig. 1f, the CNFs are visible inside the nano-necklace of silica and cellulose. The whitish lines inside the silica–cellulose hybrid is the interfacial region between the surface of the CNF and the silica, and is visible due to a lower specific density of the material in this region. Silica nanoparticles have been reported to show a density of ca. $2 \text{ g}/\text{cm}^3$,⁴¹ whereas CNFs from bacterial cellulose have a density of $1.59 \text{ g}/\text{cm}^3$.⁴² Interfacial regions in the borders of particles may show as low density as $0.9 \text{ g}/\text{cm}^3$, depending on the growth conditions adopted for the condensation of the TEOS precursor.⁴³

An observation from multiple micrographs was that the silica phase appeared to embed the extracted CNFs in their separated state, which can be seen when comparing the thicknesses of the non-coated fibrils in Fig. 1d and coated fibrils in Fig. 1e and f. The average diameter of the coated fibrils (visible through the silica particles) was 15–20 nm, whereas the CNFs in Fig. 1d showed an average of 30–40 nm. This observed size difference was related to the uncoated fibrils strong tendency to organize in bundles of 2–4 fibrils and also their tendency to become strongly associated with the carbon

surface of the grid, making them appear wider (thicker). The arrow in Fig 1 d points at one of these bundles that consists of at least 2 fibrils and shows that the fibrils appear thinner when crossing the vertically positioned bundle of fibrils at the right side of the micrograph as it was lifted from the surface of the grid at this particular point.

3.2 Reaction conditions for efficient silica coating

Fig. 2 a to c show the relevance of selecting the proper reaction medium composition on the overall outcome of the precipitation of silica in the vicinity of the CNFs. In all the experiments, the amounts of CNFs, TEOS and ammonia were kept constant. When methanol was used as main solvent, a uniform formation of coating on the CNF surfaces' did not occur. Only occasionally, small sub-10 nm grains could be observed on the surface of the fibrils and the majority of the condensed TEOS was present as poorly structured silica gel (sub-5 nm particles) separated from the CNFs (see Fig. 2a). This sort of nanostructured silica gel was previously reported in a more concentrated state as matrix for the preparation of silica-cellulose aerogels⁴⁴. Fig. 2b shows the result of using ethanol instead of methanol, which resulted in significantly increased size of the silica particles and proper condensation onto the fibrils surfaces. However, the randomly organized particles along the fibrils and their poor coverage in combination with the observed size difference indicated a very heterogeneous formation of the silica phase in the ethanol-based solution. A further increase in the alkyl chain of the alcohol (i.e. by changing ethanol to 2-propanol) resulted in a more homogeneous morphology, Fig 2c. All fibrils were completely covered as cores in silica shells, which consisted of half-spheres of silica that had grown together by the condensation occurring at the later stages of the reaction.

The effect of the alcohol chain length (namely, the molecular weight) on the size/morphology of the silica particles/network can be mainly attributed to the different relative permittivity ϵ (dielectric constant) of the alcohols. With reference to our system, ϵ scales inversely with the molecular weight of the alcohol used, equalling 32.6, 24.55, and 18.3 for methanol, ethanol, and 2-propanol, respectively. The use of methanol as a solvent resulted in an increase in the rate of hydrolysis due to the higher polarity and the smallest steric hindrance compared to that of the other solvents, i.e. ethanol and 2-propanol^{39, 45}. The high hydrolysis rate for the methanol-based system explained the poorly structured, grainy network formed in the vicinity of the cellulose fibrils. As observed in other TEOS systems, an increase in the hydrolysis rate may also yield branched morphologies of the final silica network rather than spherical particles⁴⁶. On the other hand, the more sterically hindered longer-chain 2-propanol provided a lower hydrolysis rate, limited the nucleation rate, and promoted growth directly on the cellulose surface. This was explained by the fact that the hydrolysed TEOS ($\text{Si}(\text{OH})_4$) concentration never exceeded the critical limiting super saturation concentration, thus only growth onto already formed surfaces occurred.^{39, 47-49}

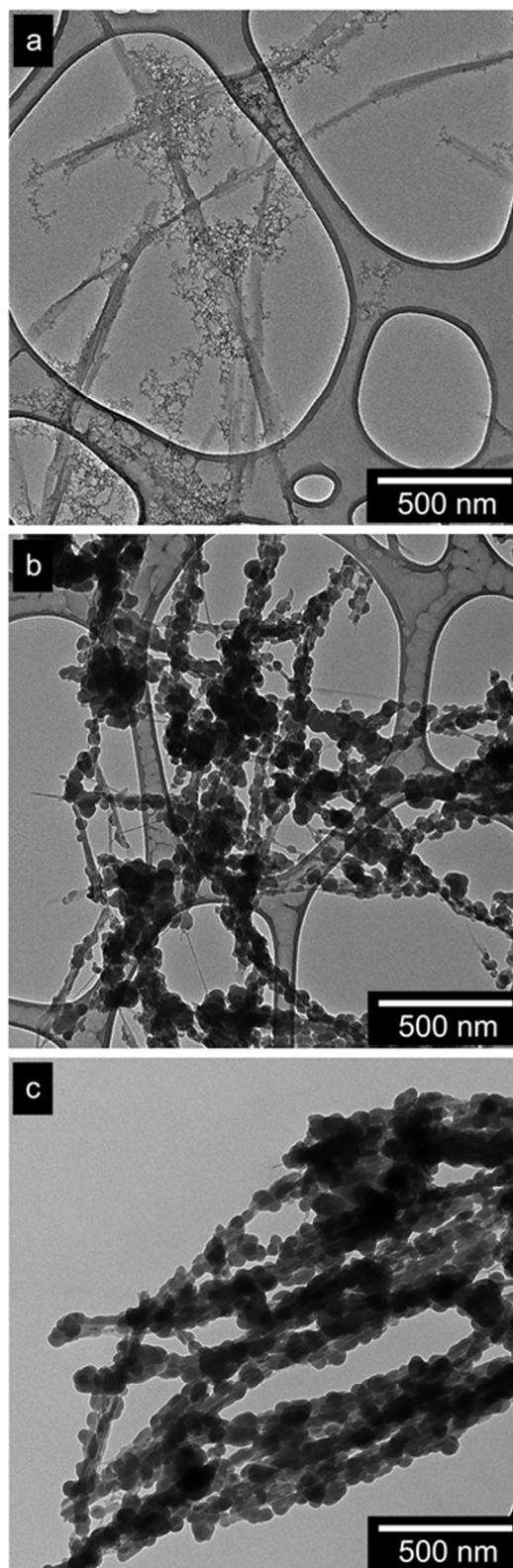


Fig. 2. Micrographs showing the effect of reaction medium on the precipitation of the same concentration of silica in the vicinity of CNFs. Reaction medium: a. methanol; b. ethanol; c. 2-propanol. The amount of water was 25 wt.% in all cases.

It is apparent from the results that the alcohol configuration had the most dominant effect on the condensation chemistry in the presence of the CNFs. It was also observed that the ammonia concentration had essentially small effect on the formation of the silica, only showing a slightly more even distribution for the highest concentration applied, see suppl. info Fig. S2. All further characterization was therefore focused on the fibrils coated in the 2-propanol solutions.

3.3 Thermal properties of silica coated CNFs

Fig. 3a and b shows the thermal behaviour of the silica coated CNFs as compared to uncoated CNFs in nitrogen and oxygen. The presence of different silica coverage on the CNF surface increased the onset of the degradation temperature with ca. 50 and 70 °C under nitrogen (to 315 and 335 °C) for the semi-complete (3 mg/mL) and the complete (1 mg/mL) coverage, respectively, from 265 °C for the uncoated CNF (under nitrogen), Fig. 3a.

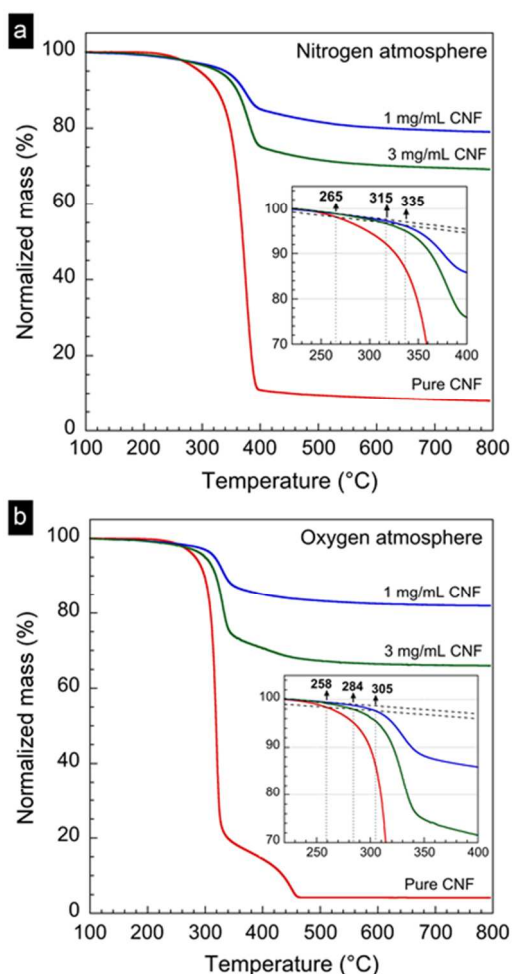


Fig. 3. TGA curves of silica-coated CNFs, (a) under nitrogen atmosphere, (b) under oxygen atmosphere. All samples were run 3 times to ensure accuracy in the plotted data. 1 and 3 mg/mL refers to the concentration of CNFs in the reactions.

The same trend was observed for the samples heated under oxygen but with smaller increase in the degradation stability,

i.e. 25 and 47 °C from 258 °C (semi- and complete coverage), Fig. 3b. Table 1 shows a summary of previously highest reported temperatures of onset and maximum mass loss rate for cellulose nanofibrils, as compared with the silica shell-covered CNFs. The temperature for the onset of the degradation was defined as the temperature where the materials had lost 1 wt.% mass as determined from a fitted straight line drawn from 150 to 200 °C for each TGA sample (to eliminate possibly strongly bound crystalline water)¹⁴.

Cellulose	Extract. media	Atm.	Onset temp (°C)	Max mass loss temp (°C)	Ref.
Wood pulp	ClCH ₂ CO ₂ H	N ₂	249	335	1
Cotton	H ₃ PO ₄	Air	276	326	2
Cotton	HCl	Air	269	350	2
Bacterial CNFs (BC)	H ₂ SO ₄	N ₂	263	332	3
Core-shell CNFs (BC)	HCl	N ₂	335	377	This work
Core-shell CNFs (BC)	HCl	O ₂	305	331	This work
Kenaf	HCl	N ₂	264	358	6
Wheat straw	HCl	N ₂	229	344	11
Sisal	H ₂ SO ₄	N ₂	254	348	7
Agave tequilana	H ₂ SO ₄	Air	231	321	8
Rice husk	H ₂ SO ₄	N ₂	229	263	9
Ramie	H ₂ SO ₄	He	258	337	10
Tunicate	H ₂ SO ₄	N ₂	276	363	4
Microcrystal	H ₂ SO ₄	N ₂	252	308	5

Table 1. Data from previous articles were obtained by digital reading of scanned plotted values in graphs. Definitions of temperature zones were according to main text.

The complete silica coverage of the CNFs also resulted in an increase in the maximum mass loss-rate temperature to ca. 377 °C from the 374 °C (under nitrogen), and to ca. 331 °C from 320 °C (under oxygen). The small difference in maximum mass loss rate temperatures compared to that of the onset of the degradation temperatures indicated that the silica coating on the CNFs was not able to prevent the bulk degradation once it started, even for the thickest coatings. The values for the maximum mass loss rate temperatures were therefore regarded as less useful for comparisons of degradation stability, and from an engineering point of view the maximum temperature the material can withstand will be better represented by the onset of the material degradation.

The residual SiO₂ mass for the samples allowed for calculating the coating reaction efficiency and the 0.06 mL (0.27 mmol) of used TEOS should convert into 16.1 mg of SiO₂ assuming 100 % efficiency. Considering the total weight of cellulose (2.7 mg and 8 mg), the reactions should therefore result in a SiO₂ content of 85.7 and 66.8 wt.% of the hybrid

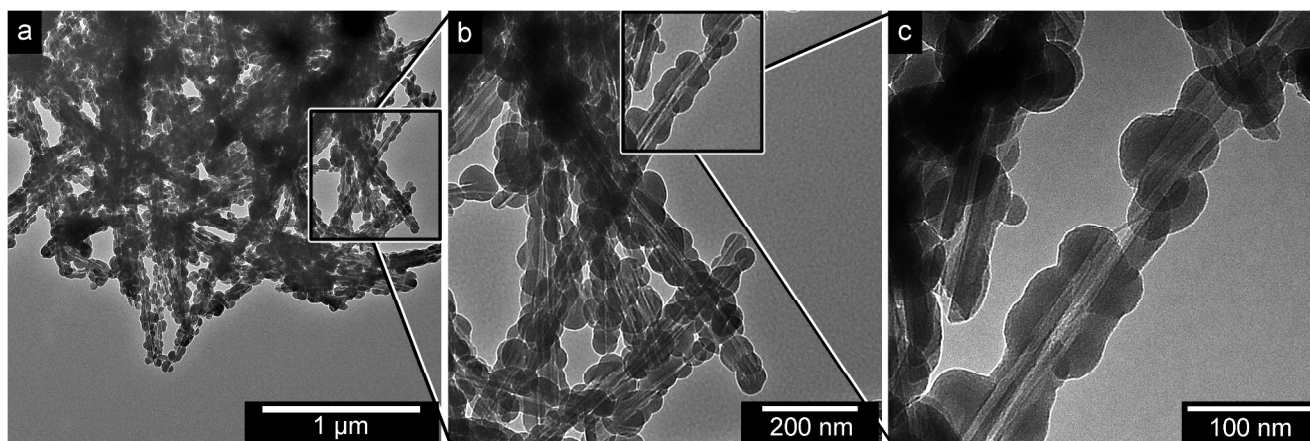


Fig. 4. Transmission electron micrographs of the silica remain after oxygen degradation of the cellulose nanofibril interior (a–c).

fibres. The mass loss (Fig. 3b) showed that the final SiO₂ content (deducting the mass of residual ash) after ultra-sonication and washing was 80 and 65 wt.% for the two concentrations of coated fibres. This corresponded to a yield for the coating procedure of 93 and 97 % for the 1 and 3 mg/mL system, confirming that the silica condensed in-situ on the surface of the fibres. Hence, only a small amount of silica was lost in the entire processing (incl. ultra sonication/washing of the fibres).

An unexpected observation from the measurements can be seen in Fig. 3b, which shows that the degradation of the uncoated fibrils (oxygen) slowed down considerably as 80 wt.% of the material was degraded at 320 °C, and complete degradation was not reached until at a temperature of ca. 460 °C. It is suggested that this transition was due to extensive formation of char at the surface of the sample, which restricted the accessibility of the oxygen.^{13, 50} This phenomenon was not observed for the identical fibrils degrading under nitrogen at ca. 50 °C higher max mass loss rate temperature, i.e. 374 °C (Fig. 3a). Instead the degradation pattern showed a more continuous weight-loss, which may have included both degradation mechanisms visible as separated mass-loss occasions in Fig. 3 b. The residuals left in the crucibles after the heat treatment in nitrogen atmosphere was ca. 8 wt.% black char, whereas the oxygen conditions resulted in ca. 4 wt.% white char. The black char was therefore interpreted as a sign of incomplete transformation of the carbon material into carbon dioxide. It is suggested that the presence of extensive amount of ‘capping’ char, in combination with the very low (ppm) amounts of oxygen in the nitrogen gas, was the explanation to the continuous weight loss up to 800 °C for the sample degrading under nitrogen. This behaviour indicated that the major role of the silica phase was similar to the ‘capping’ char in that it prevented the diffusion of oxygen into the cellulose fibrils, and limited the outgassing of degradation products, thereby delaying the degradation of the cellulose.

3.4 Silica and char residuals post high-temperature treatment

The silica–cellulose fibril residuals collected from the TGA crucible after the high temperature treatment in oxygen are shown in Fig. 4. The cellulose had been completely removed (see XRD, suppl. info. Fig. S3), and all internal structural support from the CNFs was eliminated. Fig. 4c shows that the hybrid silica/cellulose fibrils had been converted into hollow silica nanotubes. The results also confirmed that the silica coatings before the heat treatment were completely covering the CNFs. Seldom, the silica nanotubes appeared broken at their ends where poor silica fibril coverage had been the case, i.e. leaving open tube morphologies (see Fig. 4c). The most frequent endings were spherical shaped particles that had nucleated at the end points of the removed fibrils (see Fig. 4b). The brighter interior of the nanotube in Fig. 4c also shows that the conformation of the CNFs inside the coated hybrid fibres were dominantly as bundles. The ca. 30 nm width of the removed fibril bundle was consistent with a coating deposited on 2–3 CNFs, as discussed in section 3.1.

3.5 Hybrid fibre aerogels and their high-temperature behaviour

Figure 5 shows that the hybrid silica/cellulose fibres could be formed into aerogels by simple freeze-drying, Fig 5a (right image). The macroscopic appearance of the hybrid foam was similar to the pure cellulose foam (Fig. 5a, left image) whereas its mechanical integrity was higher (easier to handle) and more shape-precise to the mould used when freeze-drying the cubes. The densities of the solid cubes were 0.005 g/cm³ in both cases based on the weight and volume of the cubes. The photographs in b and c show the result of the cellulose phase degradation when the foams were heated from room temperature to 400 °C (heating rate: 20 °C / min). Whereas the pure cellulose aerogel lost more than 99.9% of its volume, the hybrid foam was indifferent in shape even if the embedded cellulose had been completely degraded. The intact shape of the hybrid foam was due to the presence of a remaining uniform and intact network of the silica nanotubes.

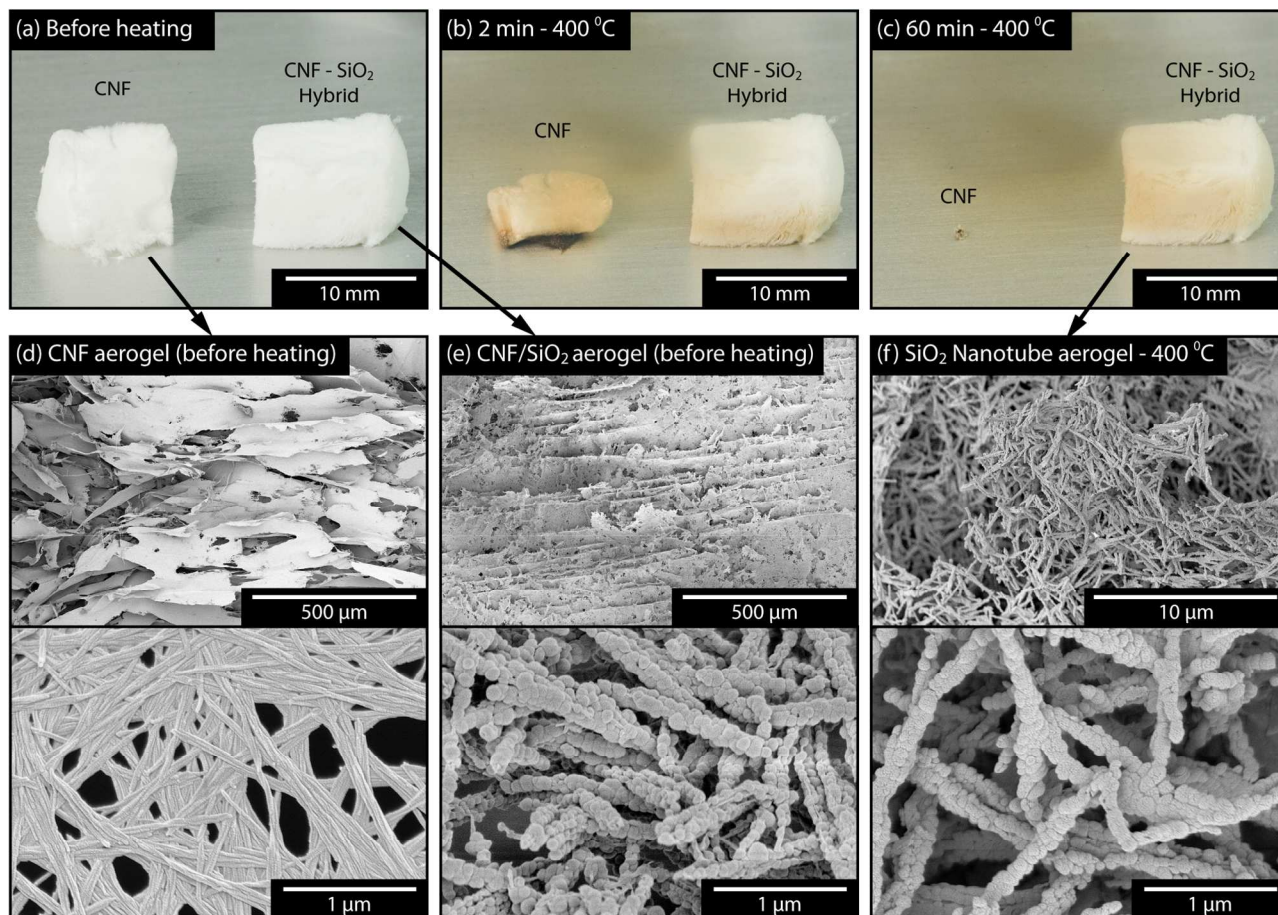


Fig 5. Photographs with corresponding scanning electron micrographs of the cellulose, hybrid silica/cellulose and silica nanotube aerogels at different stages during transformation.

Fig. 5d-f shows the wall structures of the foams before and after the heating experiment. In both cases the macroscopic organisation of the walls was dictated by the ice crystals formed during the quenching of the fibre suspensions in a similar manner as reported in the preparation of cellulose-based biofoams.^{5,51} The lower images show that the in-situ condensed silica particles, which entirely cover the cellulose nanofibrils, prevented their inter-condensation into sheet-like flats visible in Fig. 5d, compare Fig. 5e for the hybrid material. From Fig. 5f it was clear that even in absence of the fibrillar inter-condensation the aerogel structure remained after removal of the cellulose phase. Cellulose silica composites have previously been demonstrated by a few research groups,⁵²⁻⁵⁴ however, so far the fabrication of these from fully embedded individual cellulose fibrils that can be used as building blocks for silica nanotube aerogels, or as more thermally stable fibrils for liquid processing, has not been reported. A time-lapse video on the thermal degradation and collapse of the cellulose aerogel compared with the silica hybrid aerogel is included in the supplementary information section (suppl. video 1), showing that the hybrid material retains its shape even after conversion into silica nanotubes at 400 °C.

4. Conclusions

A key parameter for growth of solid silica layers on the surface of cellulose nanofibrils is to use a reaction medium that permits in-situ nucleation on the surface of the fibrils, i.e. by avoiding premature silica nucleation in the reaction medium. The quantity of silica precursor for proper nucleation and growth on the surface of the CNFs is required to meet with the reactive surface of the CNFs (which can be established by dilution experiments). The results show that under these premises it is possible to realize an average efficiency of the entire coating procedure of ca. 95 % yield (including the coating reaction combined with ultra-sonication and washing). The coated fibrils were present as individual fibrils, or bundles of 2-3 CNFs that remained from a limited separation during the extraction of the CNFs. A full silica coverage on the CNFs limited the accessibility of oxygen and restricted degassing of degradation products, resulting in delayed CNF degradation. The shifts in the onset mass loss temperature to higher temperatures were ca. 70 °C for N₂ and 50 °C for O₂. Complete CNF degradation/pyrolysis allowed for preparation of hollow silica nanotubes.

It is also demonstrated that the core-shell structured CNF-silica hybrid fibres allowed for simple freeze-drying to be used to prepare mouldable silica cellulose aerogels. Here, the slender CNF network penetrating the aerogel served as a structural support, which prevented collapse of the aerogel during the

drying. The CNF-silica hybrids aerogels could further be converted into silica nanotube aerogels by simple heating to 400 °C (video available in ESI). The preparation scheme may open up for large-scale fabrication of silica aerogels for thermal insulation, which traditionally has been relying on super critical drying methods.

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Notes and references

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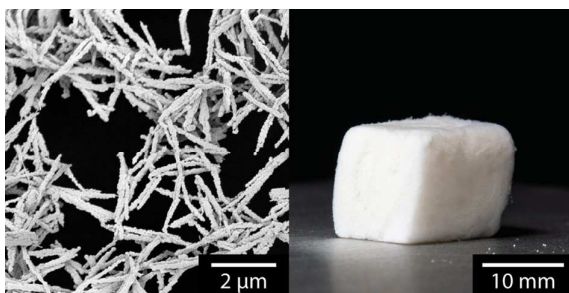
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† Electronic Supplementary Information (ESI) available: Video portraying the formation of silica nanotube aerogels on the degradation of cellulose nanofibrils template. X-Ray diffraction showing the elimination of the cellulose fibril support used to prepare the silica nanotube aerogels.

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Thermally stable, ultra-low density, silica-nanotube-based aerogels created *via* templating from cellulose nanofibrils without relying on energy intensive supercritical drying.