Inorganic Hollow Nanotube Aerogels by Atomic Layer Deposition onto Native Nanocellulose Templates

Juuso T. Korhonen, Panu Hiekkataipale, Jari Malm, Maarit Karppinen, Olli Ikkala, and Robin H. A. Ras

One-dimensional nanostructures with lateral dimensions below 100 nm, including nanowires and nanotubes, are a technologically important class of materials with unique thermal, electronic, optical, and mechanical properties, and they are feasible in applications as nanoscale building blocks for functional materials and devices. Inorganic nanowires, for example, have spurred research toward single-molecule detection, energy harvesting, nanoelectromechanical systems, and detection of neural signals. Inorganic nanotubes have been pursued in optoelectronics, sensors, drug release, and fluid manipulation. During recent years, many routes toward hollow inorganic nanomaterials have been demonstrated, including templating on nanoporous membranes or nanofibers, for example, coating anodic aluminia membranes by various methods, directly anodizing titanium dioxide films, coating electrospun fibers, and coating block copolymer templates with inorganics. In this context, also aerogels could be particularly useful as facile highly porous network-like solid templates for inorganic nanotubes.

Highly porous solid materials, called aerogels, were first discovered in the 1930s, and although silica aerogels were commercially produced already in the 1940s, it was not until late 20th century when a more broad range of applications was introduced. Nowadays several types of aerogels are made by sol–gel chemistry. In addition to silica, aerogels can be made from several different materials, such as polymers (including cellulose), which can then be pyrolyzed to carbon aerogels. Also metals and metal oxides, such as aluminum oxide and zinc oxide, have been used to form aerogels.

Cellulose is an interesting sustainable and natural polymer. Native cellulose forms a hierarchically ordered material, where the individual cellulose polymer chains first crystallize into nanofibrils of ca. 3–15 nm diameter, which then pack into larger fibers of several tens of nanometers, and finally into macroscopic fibers of micrometer dimensions. The native nanofibrils can be cleaved by several ways to form nanocellulose hydrogels. Usually the material is called nanofibrillated cellulose (NFC) or alternatively microfibrillated cellulose (MFC). While NFC is interesting in itself, it is also attractive as a biological template for functionalities. Nanocellulose hydrogels can be dried to form percolating networks, that is, aerogels, and then in turn be pyrolyzed to carbon polymers (including cellulose), which can be deposited to form a porous framework consisting of inorganic hollow nanotubes. First we show a preparation method for titanium dioxide, zinc oxide, and aluminum oxide nanotube aerogels based on atomic layer deposition (ALD) on biological nanofibrillar aerogel templates, that is, nanocellulose aerogels without major interbrillar aggregation even in thick films. Uniform oxide layers are readily deposited by ALD onto the fibrils leading to organic—incorporated—shell nanofibers. We further demonstrate that calcination at 450 °C removes the organic core leading to purely inorganic self-supporting aerogels consisting of hollow nanotubular networks. They can also be dispersed by grinding, for example, in ethanol to create a slurry of inorganic hollow nanotubes, which in turn can be deposited to form a porous film. Finally we demonstrate the use of a titanium dioxide nanotube network as a resistive humidity sensor with a fast response.

KEYWORDS: microfibrillated cellulose (MFC) · nanofibrillated cellulose (NFC) · chemical vapor deposition (CVD) · nonwoven fiber · nanofiber
by going around the critical point of the medium (i.e., supercritical drying).

In this work we made nanocellulose aerogels by three distinct methods: (a) freeze-drying in liquid nitrogen (at boiling point $-196 \, ^{\circ}C$) or (b) in cooled liquid propane (boiling point $-42 \, ^{\circ}C$, cooled to $-100 \, ^{\circ}C$) followed by ice sublimation in vacuum, or (c) supercritical CO$_2$ drying. For comparison, we made a sample by (d) evaporation of liquid water from nanocellulose hydrogel under ambient conditions. A comparison between the preparation techniques is summarized in Table 1, and scanning electron microscopy (SEM) micrographs of the observed structures along with a summary of the preparation methods are shown in Figure 1 (see Supporting Information Figures S2—S4 for higher resolution micrographs).

Freeze-drying by freezing the nanocellulose hydrogel in liquid nitrogen followed by sublimation of ice in vacuum results in large sheetlike aggregates, which are connected to each other by cellulose fibrils. Large pores can be seen to form on the top of the film. It has been proposed that the sheets and pores result from growing ice crystals pushing the fibrils into sheets, which then meet at the interfaces of the crystals. Liquid propane cooled well below the boiling point is more efficient in transferring heat than liquid nitrogen, because it does not boil when the hydrogel is immersed in it. The Leidenfrost effect, that is, the formation of an insulating gas layer, is suppressed, and thus plunging thin hydrogel samples into liquid propane leads to nearly instant freezing. Therefore ice crystals are smaller and the original nanofibrillar network structure is better preserved upon freezing and sublimation of ice. The resulting structure consists mostly of small fibrils with only few fibril aggregates. Note that there are no sheets formed in contrast to the liquid nitrogen freeze-drying, and the structure is similar throughout the film with essentially no aggregation up to about 2 mm thick films. However, increasing the film thickness further will eventually lead to sheetlike aggregation and “cell” formation in the center of the film where the two ice crystal fronts meet (cf. Supporting Information Figure S3). Because of different thermal expansion for the substrate and the film, there can be cracks in thick films. Supercritically dried samples are fibrillar throughout over 15 mm thick samples and no clear aggregation to sheets is observed. Also no cracks exist in the monoliths. Although

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**TABLE 1. Comparison among Different Aerogel Preparation Methods**

<table>
<thead>
<tr>
<th>method</th>
<th>structure</th>
<th>aggregation</th>
<th>observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>a freeze-drying by immersion in liquid nitrogen and ice sublimation</td>
<td>aerogel</td>
<td>sheetlike aggregates</td>
<td>aggregation can occur in thick samples</td>
</tr>
<tr>
<td>b freeze-drying by immersion in liquid propane and ice sublimation</td>
<td>aerogel</td>
<td>no aggregation in thin samples</td>
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<tr>
<td>c supercritical CO$_2$ drying from acetone organogel</td>
<td>aerogel</td>
<td>no aggregation</td>
<td>no aggregation in thick samples</td>
</tr>
<tr>
<td>d drying under ambient conditions</td>
<td>collapsed</td>
<td>sheets parallel to substrate</td>
<td>paper- or plastic-like appearance</td>
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they have been prepared from chemically modified, solubilized, and native cellulose by supercritical drying and freeze-drying. Typically cellulose aerogels have suffered from brittleness, but the native cellulose aerogels have shown attractive mechanical properties, ductility, and flexibility. This has encouraged development of aerogels with electrical, optical, and magnetic functionalities.

Atomic layer deposition (ALD) is a sequential, self-limiting chemical vapor deposition method, which enables control of the deposited thickness by the number of cycles instead of the deposition time. The gaseous ALD precursors are released into a sample chamber one at a time and then allowed to react with the surface groups of the sample before the reaction byproduct and unreacted precursor molecules are purged from the chamber. The second precursor is then introduced and the cycles are repeated until the desired film thickness is reached. A unique characteristic of ALD is that it forms very uniform films with almost atomic precision on planar substrates but also on complex three-dimensional porous substrates, because the sequential reactions allow long diffusion times for the precursors. ALD usually employs lower temperatures than normal chemical vapor deposition. The deposited materials are mostly oxides, but also metals, nitrides, polymers and organic–inorganic hybrid materials have been prepared.

Here we describe a facile method for preparation of hollow inorganic nanotubes by coating nanocellulose aerogels with different oxide materials using ALD, followed by temperature-induced decomposition of cellulose, that is, calcination. As a demonstration for functionality, we show that a film made from TiO$_2$ nanotubes acts as a resistive humidity sensor with relatively rapid response times.

**RESULTS AND DISCUSSION**

Comparison of Aerogel Preparation Methods. Nanocellulose hydrogels (see Materials and Methods) can be dried to form aerogels provided that collapse of the fibrillar structure is avoided. Collapse normally occurs during water evaporation because capillary forces pull the fibrils together. Crucial to aerogel preparation is to avoid the direct liquid-to-gas phase transition, by going around the transition line either through liquid-to-solid and solid-to-gas transitions (i.e., freeze-drying) or...
the solvent exchange process is slow, supercritical drying is worthwhile if highly fibrillar aerogels without aggregation are wanted. A potential drawback of supercritical drying is that the water in the hydrogel cannot be directly exchanged to CO2, but instead intermediately has to be exchanged to an organic solvent (here to acetone) to form an organogel. The organic solvent has to be selected such that it mixes well both with water and CO2 and that it does not significantly modify the network structure of cellulose fibrils. Finally, letting the water freely evaporate from the hydrogel leads to a collapsed thin film of nanocellulose. A close-up reveals some single fibrils, but in general the structure is very dense and consists of sheets mostly parallel to the substrate.

**Inorganic—Organic Aerogels by Atomic Layer Deposition onto Nanocellulose Aerogel Templates.** Zinc oxide (ZnO), titanium dioxide (TiO2), and aluminum oxide (Al2O3) were deposited on the fibrillar nanocellulose aerogels, and they formed uniform inorganic layers on the fibrils as seen in Figure 2. Even though cellulose aerogels are reported to withstand temperatures up to 275 °C,176 we observed slight yellow color on the surfaces of the samples after deposition. The growth-per-cycle (GPC) values of the ALD processes were determined from the thicknesses measured using transmission electron microscopy (TEM). The initial layer thickness value is the thickness where the growth saturates when the first pulse of precursor is fed into the sample chamber. The growth of a few nanometer thick inorganic layer on nanocellulose upon a single pulse of titanium isopropoxide was reported recently.40 Our initial layer thickness was mostly dependent on how well the sample was dried before the deposition process, and all values were 0–3 nm as a result of careful drying. The GPC values were between 0.09 and 0.11 nm for all precursors. To ensure that the initial layer growth was saturated after the first precursor pulse, a sample was further exposed to two subsequent long pulses of the precursor. No differences in the layer thicknesses were observed between these two samples, which in turn supports that the initial layer growth had saturated before the first pulse was over. SEM and TEM images of the coated aerogels show that there were differences between the different oxides. While Al2O3 and TiO2 allowed very uniform and smooth layers, ZnO lead to a more rough coating due to crystallite formation. In all cases, the fibers have not
fused together to form sheets or other larger aggregates (cf. Supporting Information Figure S5), but they represent a coated replica of the original aerogel structure.

**Inorganic Hollow Nanotube Aerogels.** The cellulose cores of the coated aerogels were easily removed by calcination at 450 °C under air for an extended period of time to form hollow inorganic tubes. The material contracts slightly, which can lead to cracks on the film, but even large samples are still self-supporting, although unlike the pristine nanocellulose and ALD-coated nanocellulose aerogels, they are brittle. SEM reveals the hollow structure (Figure 2), where the inner diameter depends on whether there was an individual cellulose fibril or a bundle of fibrils on the template. Al2O3 creates very uniform coatings on the fibrils, which are preserved upon calcination, while the TiO2-coated fibers crystallize during the calcination. Zinc oxide shows a rough surface already after the ALD process, and it is even more pronounced after calcination. The structure of the aerogel is well preserved after calcination.

**Dispersed Nanotubes.** The inorganic nanotube aerogels can be crushed in a mortar and dispersed, for example, in ethanol to create a slurry of hollow nanotubes, where the nanotubes form aggregates, which have a porous aerogel-like structure upon solvent evaporation. The size of the aggregates in the slurry can be controlled by sonicating and by mechanical grinding, and from the slurry it is easy to dropcast films of hollow nanotubes onto substrates. We casted TiO2 nanotube films with thicknesses ranging from 5 to 50 μm on fluorine tin oxide (FTO) coated glass substrates (see Figure 3).

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**Figure 2.** SEM (a-f) and TEM (g-i) of ALD coated aerogels. The number of ALD cycles is indicated in each figure. (a) A thin uniform ZnO layer formed on nanocellulose fibrils after initial exposure to the zinc precursor. (b) ZnO layer thickness is increased upon the ALD process (here 50 cycles). (c) Calcinated, hollow ZnO nanotubes are visibly rough. (d) Close-ups on ZnO nanotubes show that they are hollow. (e) TiO2 nanotube aerogel. (f) Hollow Al2O3 nanotube aerogel. (g) A hollow TiO2 nanotube, showing some roughness due to crystallization. (h) A hollow Al2O3 nanotube demonstrating smooth uniform coating. (i) A hollow ZnO nanotube has undergone crystallization, making the hollow tube interior difficult to resolve. The inset shows a ZnO-coated fibril before calcination. (j) An intensity profile across a hollow TiO2 nanotube. (k) An intensity profile across a hollow Al2O3 nanotube.

**Figure 3.** Films cast from a crushed hollow TiO2 nanotube dispersion in ethanol. (a) Photographs of a 15 μm (left) and 25 μm (right) thick films. Film dimensions are 5 × 8 mm. (b) Tilted SEM image shows that the TiO2 film (ca. 50 μm thick) with only a few cracks has formed on the substrate. (c) Larger magnification shows the edge of the film. The film consists of granules of micrometer dimensions. (d) High magnification image shows that the granules are formed of networks of TiO2 tubes. (e) Energy dispersive X-ray spectrum shows that there is only very little carbon in the film and the TiO2 content is high. Other peaks originate from the FTO glass.
Photographs of dropcast TiO$_2$ films show that the films have formed smoothly on the substrate and only a small amount of cracking is observed (Figure 3). Higher magnification images show that the aggregates are micrometer sized and they consist of a porous network of TiO$_2$ nanotubes. Energy dispersive X-ray (EDX) spectrum taken from top of the film shows large titanium and oxygen peaks, while the amount of carbon can be calculated to be less than 1% by weight, which confirms that the organic core has been emptied by thermal decomposition of cellulose into small gaseous molecules such as carbon dioxide and water. The gases can diffuse out from open tube ends, but may also pass through the ALD-grown inorganic coating, similar to what has been observed for ALD-coated polymeric nanorods.$^{12}$ The other peaks observed in the EDX spectrum are from either the glass substrate or the FTO layer on the glass. The crystalline structure of the TiO$_2$ nanotubes was assessed by X-ray diffraction (XRD). From the patterns we identified that there is mostly anatase (see Supporting Information), which is expected after the calcination.

**TiO$_2$ Nanotube Film as a Humidity Sensor.** Nanowires have been amply demonstrated based on different semiconducting nanowires between two electrodes.$^{53-55}$ It is interesting to explore whether particularly simple TiO$_2$ nanotube sensors could be constructed based on nanotubes by ALD on nanocellulose templates and subsequent calcination. Measuring conductivity of a dropcast TiO$_2$ nanotube film reveals a dependence of resistance to the humidity of the environment. The humidity sensitivity of dropcast TiO$_2$ nanotube films was tested in air and argon atmosphere and the electrical response between two electrodes was reproducible. The response of resistance and capacitance to humidity is shown in Figure 4. From relative humidity of 0–40% there was barely any change in resistance, but going from 40 to 80% the resistance decreased to 1/30th of the original value. The response is linear on a logarithmic scale with respect to the relative humidity. A similar increase in capacitance over the same region was also observed. Both of these changes were reversible. After prolonged exposure to a dry atmosphere the samples had a higher resistance, but they returned to the reversible curve after being exposed to humidity.

In the TiO$_2$ nanotube films, some tubes form continuous paths from electrode to electrode while others are dead ends. We assume that the dead ends contribute to the capacitance of the film and the current flows through the continuous network. The change in resistance upon humidity can be tentatively explained simply by the water adsorbed on the surface of the tubes, which can increase the conductivity of the system. Because there is a high surface area on the tubes, the effect of surfaces and adsorption is pronounced compared to flat films. The change in capacitance could be addressed to change in the dielectric constant, $\varepsilon$, of the insulating medium. Water has higher $\varepsilon$ than any of the gases and the capacitance of a simple plate capacitor is of the form $C \propto \varepsilon$, therefore the capacitance would increase with increasing humidity, as observed. Figure 4 also shows that the voltage response of a TiO$_2$ nanotube film (at steady current) is correlated with the humidity of the chamber. We assume a simple exponential shape $U(t) \propto e^{-t/\tau}$ for the response with a time constant $\tau$. The response to humidity was very rapid with a time constant...
r\text{\textsubscript{aw}}\text{ less than } 2 \text{ s. Simply by breathing out humid air on top of the sample, a decrease in applied voltage is observed due to the local humidity increase. A reverse behavior was observed when a sample was blown with pressurized dry air. In this case } r\text{\textsubscript{aw}}\text{ was ca. 14 s.}

There have been a few reports on neat TiO\textsubscript{2} films or nanostructures acting as humidity sensors.\textsuperscript{53,54,56} Zhang et al. reported a resistive humidity sensor from a TiO\textsubscript{2} nanotube array, and it was tested with different calcination temperatures.\textsuperscript{54} The calcination temperature affects the crystal form of TiO\textsubscript{2}, and rutile form provided the best results for sensing. A sample calcinated at 600 °C gave the best response with response times of 100 and 190 s for dry (5%) and humid (95%) air. Our response times are 10–100 times faster than these values. Steele et al. made a rutile TiO\textsubscript{2} humidity sensor with subsecond response times,\textsuperscript{56} but their sensor is capacitive and it is not based on nanowires or nanotubes. For comparison, the commercial Vaisala humidity meter we used as reference has a reported response time of ca. 8 s.

**CONCLUSION**

We have demonstrated a facile route for preparation of hollow inorganic nanotube aerogels based on ALD on native nanocellulose aerogel templates and removal of the template by calcination. Nanocellulose aerogels were prepared by freeze-drying and supercritical drying. Different drying methods were compared: liquid nitrogen freeze-drying leads to sheetlike aggregation, liquid propane freeze-drying enabled fibrillar structures up to sample thicknesses of ca. 2 mm, whereas supercritically dried aerogels showed no aggregation even in centimeter thick samples. The nanocellulose aerogels can readily be uniformly coated with different inorganic oxides (ZnO, TiO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3}) by atomic layer deposition. We demonstrate that the inorganic–organic aerogel can be calcinated to obtain a purely inorganic hollow nanotube aerogel. Porous films can be prepared by dispersing the inorganic nanotubes into a solvent and then casting it on a substrate. A TiO\textsubscript{2} nanotube humidity sensor with relatively fast response times in the humidity region of 40–80% was demonstrated.

Inorganic hollow nanotube aerogel networks could have future applications in functional materials, such as nonwetting surfaces, sensors, and carriers and also in encapsulation, drug-release, catalysis, microfluidic devices, and filtration.
Characterization Techniques. Field-emission scanning electron microscopy (JEOL JSM-7500FA) was performed at 5 keV electron energy or below. The neat aerogels were sputtered with a thin layer of platinum (Emitech K950X/K850) to promote conductivity. JSM-7500FA is equipped with a JEOL energy-dispersive X-ray analysis addition with a 2E thin film window and liquid nitrogen cooled detector. A spot spectrum was taken over 2 min using 15 keV electron energy to analyze the composition of samples. Quantitative analysis was done by comparing the area of the fitted K_{\alpha} or L_{\alpha} peaks.

Transmission electron microscopy (TEM) was performed on a FEI Tecnai 12 operating at 120 kV. Dry samples were ground with a mortar and then applied on a carbon film support grid. Imaging was done in bright-field mode with slight underfocus.

Conductivity Measurements. The conductivity of TiO_2 nanotube films was measured as four-point resistance, conduction through the sample was fixed, and the voltage across the measurement probes was recorded, and the voltage across the measurement probes was recorded. To extract resistance and capacitance values, the sample was modeled as a parallel RC-circuit with Matlab and Simulink. Fitting was done using the least-squares method, and since only qualitative data was needed, the result was estimated by visually comparing the fitted result to the data. Fits were of good quality at relative humidities over ca. 40%.

Humidity in the measurement chamber was controlled by flowing a gas (air or argon) through a bubbler with deionized water and then mixing it with dry gas. Humidity and temperature were recorded with a Vaisala HMT333 logging temperature/humidity transmitter. Measurements were done in stable room temperature (22–24 °C), and the humidity was let to stabilize at least 15 min between measurements. Before the experiments, the samples were kept overnight in a dark, dry atmosphere to eliminate the effect of photoinduced wetting. Samples were also kept in the dark during the course of the humidity sensing experiment. To test the time dependence of the response, humid air was streamed straight onto the sample. The current flowing through the sample was fixed, and the voltage across terminals was recorded. Speed of response was estimated by fitting an exponential decay function to the data.

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Supporting Information Available: Inorganic layer thickness data (S1), larger SEM micrographs of single nanocellulose fibrils (S2), several samples demonstrating differences in preparation methods (S3, S4) and different coatings (S5–S7), XRD data for a TiO_2 nanotube film (S8). This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


12. Ras, R. H. A.; Kemell, M.; de Wit, J.; Ritaia, M.; ten Brinke, G.; Leskela, M.; Ikikala, O. Hollow Inorganic Nanophases and Nanotubes with Tunable Wall Thicknesses by Atomic Layer Deposition on Self-Assembled Polymeric Tem-


19. Luong, N. D.; Lee, Y.; Nam, J. D. Facile Transformation of Nanofibrillar Polymer Aerogel to Carbon Nanorods Cata-


25. Abe, K.; Iwamoto, S.; Yano, H. Obtaining Cellulose Nano-

fibers with a Uniform Width of 15 nm from Wood. Biomacromolecules 2007, 8, 3276–3278.


34. Sehaqui, H.; Salajkova, M.; Zhou, Q.; Berglund, L. A. Me-


