

Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents

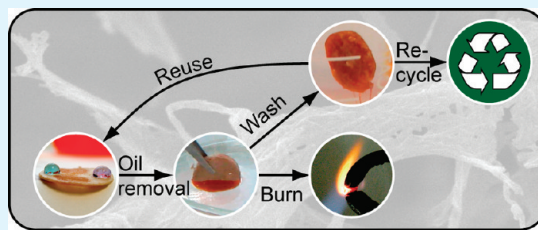
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S Supporting Information

ABSTRACT: Highly porous nanocellulose aerogels can be prepared by vacuum freeze-drying from microfibrillated cellulose hydrogels. Here we show that by functionalizing the native cellulose nanofibrils of the aerogel with a hydrophobic but oleophilic coating, such as titanium dioxide, a selectively oil-absorbing material capable of floating on water is achieved. Because of the low density and the ability to absorb nonpolar liquids and oils up to nearly all of its initial volume, the surface modified aerogels allow to collect organic contaminants from the water surface. The materials can be reused after washing, recycled, or incinerated with the absorbed oil. The cellulose is renewable and titanium dioxide is not environmentally hazardous, thus promoting potential in environmental applications.

KEYWORDS: microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), superabsorbent, oil spill recovery, atomic layer deposition (ALD), freeze-drying



Cleaning oil spills under a marine environment is a challenging task. Current methods can be divided roughly into three groups: collection of oil from the water surface; mixing of oil with water using dispersing agents to facilitate natural degradation; and in situ burning of the oil spills. The collection of oil is often preferred because this method allows proper disposal of the oil. To enhance the recovery of the oil, an absorbent material can be spread on the spill. The traditional choice is sawdust, which, however, suffers from large coincident water absorption along with the oil. Centrifugation, filtration, or simple gravitational settling is then used to separate the oil from the water to allow a larger amount to be collected.¹ For this purpose, it is attractive to develop selective materials that do not absorb water but are able to rapidly absorb a large amount of oil, that are robust, floating, reusable, recyclable and environmentally friendly, and that can be incinerated along with the oil they absorb. Here we demonstrate such a material, based on functionalized cellulose nanofibrils, where cellulose is natural, renewable, and the most abundant polymer.

Commercial polypropylene fiber mats are used for oil spill absorption^{2,3} and their oil intake can be up to ca. 15 times their original dry weight, which is ca. 50–90 mg/cm³; however, they suffer from ca. 50% retention when they are removed from the oil.³ Silica aerogels have been used to absorb oils and organic spills.^{4–6} However, it is a challenge to suppress the brittleness of the silica aerogels. Also carbon nanotubes have been grown onto vermiculite to allow oil absorption of 3–4 times vs their empty weights and oil–water selectivity of ca. 7:1.⁷ Recently, carbon nanotube aerogels have been demonstrated showing absorption capacity of 80 to 180 times vs the empty aerogel weight for various solvents and oils, owing to the very small weight of the aerogel.⁸ Manganese oxide nanofiber membranes perform as

selective absorbents and separation membranes for solvents and oils with oil intake up to 20 times vs the original weight.⁹ Although these are exciting properties, it would be desirable to identify novel widely abundant, renewable, robust, safe, and sustainable materials for environmental applications.

Nanocellulose is an attractive material for practical applications, because it is based on economic, renewable, and abundant resources and can be processed at large scale using well-established wood industry methods. Long native nanofibrils of 3–15 nm diameter can be cleaved from wood pulp by several ways to form nanocellulose hydrogels.^{10–13} Such hydrogels can be dried using vacuum-drying, freeze-drying or supercritical CO₂ drying to form highly porous nanocellulose aerogels, which can subsequently be functionalized.^{14,15} Especially the native nanocellulose aerogels have shown good mechanical properties,^{14,16,17} and they have been used, for example, for photoswitchable absorption,¹⁸ floatation,¹⁹ magnetic functionality,²⁰ and humidity sensing.¹⁵

Here we describe a nanocellulose aerogel, with a small density of 20–30 mg/cm³ and porosity of >98%,¹⁴ where the nanofibrils are functionalized with a nanoscopic layer of titanium dioxide (TiO₂) to create a hydrophobic but oleophilic coating. This functionalized aerogel absorbs a variety of organic solvents and oils, but repels water with a high contact angle. Nanocellulose hydrogel (mechanically homogenized hardwood kraft pulp, dry content ca. 2%) was vacuum freeze-dried (the hydrogel was frozen by lowering the pressure in a vacuum chamber followed by water sublimation until the vacuum level was stable at 1 × 10^{–2} mbar), as described previously.¹⁴ Images a and b in Figure 1 show

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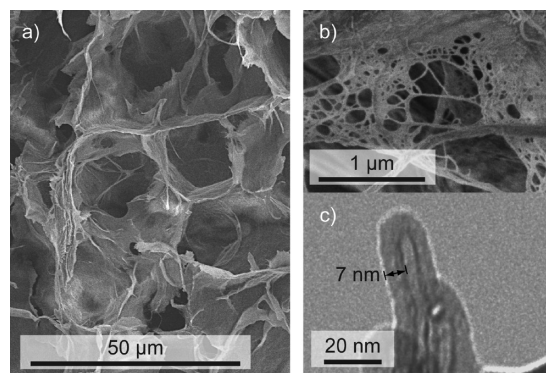


Figure 1. Microscopic structure of the native nanocellulose aerogels. SEM micrographs of (a) freeze-dried nanocellulose aerogels with fibrils packed into sheets, which are connected to form an open, porous aerogel structure, and (b) a magnification of a sheet, which is composed of fibrils making the structure also nanoporous. (c) TEM micrograph of a nanocellulose fibril with a uniform 7 nm TiO_2 coating.

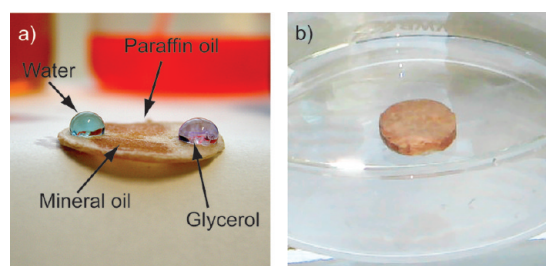


Figure 2. (a) TiO_2 -coated aerogels are hydrophobic and oleophilic: the water and glycerol stay as droplets (colored with Reactive Blue dye for clarity), whereas paraffin oil and mineral oil are readily absorbed. (b) Coated aerogel floating on water (see the Supporting Information, Video S1).

scanning electron microscopy (SEM, JEOL JSM-7500FA) micrographs of such an aerogel, where the individual nanofibrils have been forced into sheets by the growing ice crystals in the freeze-drying. The sheets are formed of individual nanofibrils, and the sheets give the aerogel increased mechanical stability.¹⁴ To achieve hydrophobicity and oleophilicity, we coated the nanocellulose aerogels with TiO_2 using atomic layer deposition (ALD, ASM Microchemistry F-120). Titanium isopropoxide was used as the titanium precursor and water as the oxygen source. A flow-through geometry along with long pulse and purge times was used to ensure a homogeneous coating also inside the aerogel. Experimental conditions and characterization have been described in detail previously.^{15,18} The first long precursor pulse formed a 2–3 nm thick uniform coating on the nanofibrils and we subsequently employed 50 titanium isopropoxide/water pulses to form a thicker layer. The transmission electron microscopy (TEM, FEI Tecnai 12) micrograph in Figure 1c shows a cellulose nanofibril, which has been coated with a uniform 7 nm TiO_2 layer. All following references to the aerogel samples refer to these TiO_2 -coated aerogels.

The TiO_2 coating on the aerogel creates a low-energy surface¹⁸ and Figure 2a shows a photograph of such an aerogel, where droplets of water and also glycerol (as another example of a polar, viscous liquid) demonstrate the hydrophobicity (contact angle $>90^\circ$) of the material, while paraffin oil and mineral oil have been readily absorbed. The oil droplets are quickly absorbed during

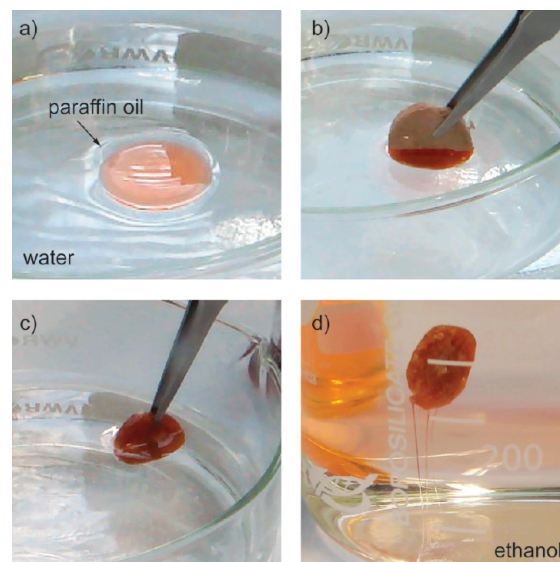


Figure 3. Oil spill removal from water (see the Supporting Information, Videos S2 and S3). (a) Paraffin oil (colored for clarity) floating on water; (b) the oil being absorbed into the aerogel; and (c) all of the floating oil has been absorbed. (d) The oil-filled aerogel can be washed simply by immersing it in a solvent, such as ethanol. The oil gets removed as shown by the red streaks.

ca. 1–3 s depending on the viscosity of the oil. Figure 2b shows the aerogel floating on water. A recent theoretical study found that the floatation of hydrophobic aerogels is mainly caused by their water repellency, whereas the low density plays only a minor role.²¹

When a hydrophobic aerogel is immersed in water, it essentially does not allow water absorption. Some water sorption, however, seemed to take place, but it turned out to be mainly due to water adhering to the surface of the aerogel due to pinning effects: we could remove the water by gently wiping the surfaces with a paper towel. On the contrary, the aerogel absorbs a large amount of oil within the interior pores from the surface of water as demonstrated in Figure 3. An oil spill with a volume almost equal to the overall volume of the aerogel is absorbed, when the aerogel is placed onto the paraffin oil spill (colored with Nile Red dye for clarity). The weight of the absorbed oil is ca. 30 times the dry weight of the aerogel. By immersing the aerogel directly into paraffin oil, up to 40 times of the original weight could be absorbed, but the excess seemed to be oil adhering outside the aerogel and wiping away the excess led to similar results as the samples absorbing oil from the surface of water. The oil-filled aerogel can be left floating on water essentially without water penetrating into the structure or oil release, as the weight of the soaked aerogel decreases only by 5% after 24 h. More than 80% of the weight decrease occurs during the first hour, which suggests that only excess oil from the surface is being removed. Floating an oil-filled aerogel on water dyed with Reactive Blue shows no color after removal, which also confirms that oil is not replaced by water (see the Supporting Information, Video S3). Furthermore, there is essentially no retention of oil when the aerogel is removed from the water as its weight remained within 95% of the wet weight after 24 h.

Importantly, the absorbed paraffin oil could be completely removed by immersing the oil-soaked aerogel into an organic solvent, such as ethanol or octane. Figure 3d shows an aerogel filled with paraffin oil dropped into a glass jar containing ethanol.

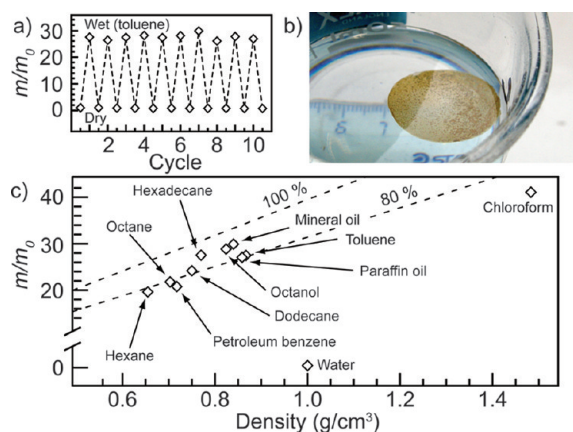


Figure 4. Demonstration of the reusability of aerogel absorbents. (a) Mass-based absorption capacity, m/m_0 , of toluene in a TiO_2 coated aerogel, where m_0 is the dry mass of the aerogel and m is the total mass. After 10 cycles there is no change in the absorption capacity or recoverability of the aerogel. (b) Aerogel immersed in toluene is translucent with some air bubbles trapped inside. (c) Plot of the mass-based absorption capacity for different organic solvents and oils as a function of the density of the liquid. The upper dashed lines represents the theoretical volume-based absorption capacity (vol/vol) corresponding to the case where aerogel is nominally completely filled with the liquid and the lower one the case where it is 80% filled.

The oil is immediately released as shown by the red streaks (note the staining). The aerogel was next immersed in ethanol overnight, taken out, and then dried. The weight difference of the dry aerogel after and before the oil immersion was very low (ca. 0.6% of the absorbed amount). Immersing the oil-soaked aerogel in octane led to even faster release of the oil and the process was complete in ca. 30 min. Experiments with mineral oil absorption and release gave the same results as with paraffin oil. The oil absorbed into the aerogel can thus be recovered by immersion of the aerogel in a suitable solvent.

To test the reusability of the aerogel we immersed an aerogel in an organic solvent (toluene) for 10 times and measured the weights before and after drying. The results shown in Figure 4a indicate that the absorption capacity does not deteriorate and the dry weight of the aerogel does not change when the aerogel is reused multiple times. In this experiment, the aerogel was dried in a vacuum oven at 60 °C for more quantitative results, but drying in ambient conditions works equally well. After this reusability experiment, the aerogel was immersed in water and it still did not absorb water, which indicates that the hydrophobicity was not lost. Figure 4b shows the aerogel immersed in toluene. Dry nanocellulose aerogels are typically opaque, but wet aerogels are translucent, which indicates that the opaqueness comes from light scattering from the fibrils. Lowering the refractive index difference between the fibrils and the surrounding medium also lowers the scattering intensity and the aerogel becomes translucent. The photograph also reveals some trapped air bubbles inside the aerogel, which slightly reduce the absorption capacity. After the cycling test, a number of different organic solvents along with some oils were absorbed and the aerogel was dried a total of 20 times without any measurable change in the dry weight or the absorption capacity indicating durability and reusability. The ratios of the final and initial weights upon full absorption m/m_0 (wt/wt) are shown in Figure 4c along with theoretical maximum lines corresponding to given constant volume (100% and 80% vol/vol plotted) intake within

the aerogel (cf. discussion below). The aerogel was dipped in organic solvents for a few seconds and about ten seconds in the oils. Arguably longer immersions times could lead to even larger intake, but qualitative visual observation showed that the aerogel was rapidly wetted. For example, the amount of absorbed paraffin oil was ca. 700 mg/cm^3 , which gives selectivity about 30:1 wt/wt compared to water, as for the same sample water adsorption was ca. 24 mg/cm^3 . Furthermore, we note that the mass-based absorption capacity m/m_0 , as used widely in literature, may not describe absorption capacity of low density absorbents adequately, because it is not constant, but increases linearly with the density of the absorbed liquid, which, in turn, is not a property of the material itself. It is also very sensitive to small changes in the density of the absorbing material. The volume-based absorption capacity, V_{abs}/V_0 (vol/vol), on the other hand, is not a function of the solvent density and may better describe the absorption capacity of the material. Our volume-based absorption capacities are 80–90% for most of the studied liquids as shown by the dashed lines in Figure 4c. To further illustrate this issue, the present aerogels are compared to the carbon nanotube sponges described by Gui et al.⁸ The volume-based absorption capacity is given by a simple equation $(V_{\text{abs}})/V_0 \cong (m/m_0) - (\rho_0/\rho_{\text{abs}})$, where ρ_0 is the density of the absorbent and ρ_{abs} is the density of the absorbed liquid. A density of 5–10 mg/cm^3 was reported for the (not densified) carbon nanotube sponges.⁸ Therein, the mass-based absorption capacity ranged from ca. 90 (hexane) to 180 (chloroform), whereas the volume-based absorption capacities are 70–140% for hexane and 60–120% for chloroform. The nanocellulose aerogel presented here absorbs ca. 80% (hexane) and 70% (chloroform) by volume, although the mass-based values are lower. Therefore, almost the full aerogel volume is exploited for the absorption. It is evident that more than 100% cannot be absorbed without the material expanding and the highest values are achieved for the lowest densities. Even though lowered material density can increase the mass-based absorption capacity, it comes on the expense of the mechanical durability.

As a conclusion, we have demonstrated that hydrophobized nanocellulose aerogels achieved by coating the native cellulose nanofibrils with TiO_2 show highly selective absorption of non-polar liquids and oils when compared to water and the oils do not drain out when the aerogel is floating on water or taken out from water. The absorption is close to the overall volume of the aerogel (80–90% vol/vol) and the mass-based absorption capacity varies from 20 to 40 (wt/wt) depending on the density of the liquid. Organic liquids were readily removed by drying and oils could be washed out with a proper solvent, such as ethanol. The absorption capacity of the aerogel does not change upon repeated immersion and drying and thus the aerogels are reusable, which makes them suited for applications. The aerogels are made from cellulose, which is sustainable and can be simply incinerated along with the absorbed oil. Here the low-surface-energy coating was TiO_2 , but other inorganic coatings or surfactants could lead to similar results. Nanocellulose can be manufactured at a larger scale, and freeze-drying and ALD are also common technical processes. In conclusion, we suggest that this work paves way for nanocellulose-based oil absorbents for sustainable applications.

■ ASSOCIATED CONTENT

Supporting Information. Videos showing floatation and water repellency (S1), oil absorption (S2) from the surface of

water, and that no water is absorbed to an oil-filled aerogel (S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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