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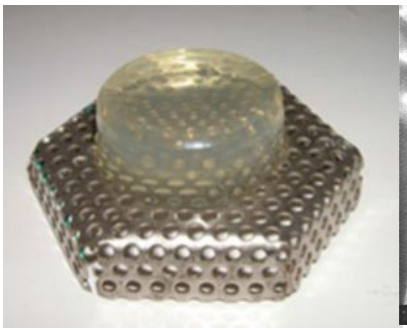
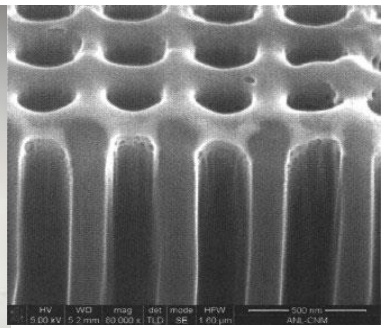
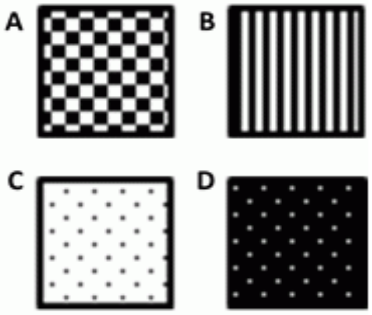
ARPA-E Challenge: Macroscopic Composites with Nanoscale Order

Hydrophobic Aerogel template with ion beam engineered hydrophilic channels







Abstract:

In order to make a macroscopic object with nanometric features it is proposed to create artificial hydrophilic channels in a hydrophobic cellulosic aerogel followed by a controlled shrinkage, filling with the desired materials and then destruction of the aerogel by oxidation treatment.

The first step is to create hydrophilic channels in a hydrophobic cellulose aerogel by ionic bombardment through a mask, thanks to the ultra-low density of the aerogel penetration of several centimeters is attainable.

Then cold hydrogen peroxide solution is poured into the channels; careful control on the temperature and pressure may permit to control the shrinkage of the aerogel to attain the desired channel radius through evaporation and also to dissolve the fibers inside the channel to obtain a truly hollow tube with dense walls.

Various possible filling strategies of the engineered aerogel template to obtain the final nanostructured object are presented.

Introduction

Building macroscopic objects with a nanoscale order is a particularly difficult task. Even if such arrangement is now possible in two dimensions, making a wafer sized piece can take weeks or months so adding a third dimension would bring the building time to several decades using standard tools.

Bottom up method may be possible in some very particular case which is not in the scope of the current challenge.

In order to build objects with such huge aspect ratio of up to two millions an easily alterable material must be found in order to build a supporting structure.

Also the said object must be destroyable at the end of the building process and leave minimal residues.

I. A possible candidate for the structural material: Cellulosic aerogel

I .1 Intrinsic properties

Cellulosic aerogels are relatively new compared to their inorganic counterparts like ones made of silica they possess characteristic aerogel properties such as extrasmall densities, hydrophilicity, high mechanical resistance, nanometric porosities and shrinking upon drying.

But in contrast to their rigid inorganic cousins they exhibit some elasticity that protect them from breakage from sudden water evaporation

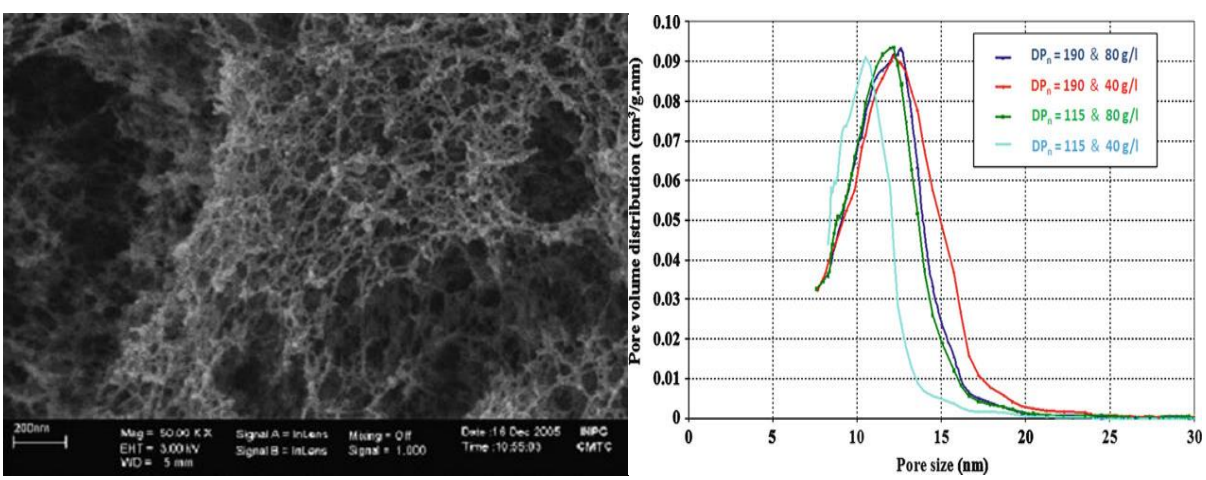


Figure 1 **source [1]**

Left: SEM-FEG microscopy of cellulose acetate-based aerogels

Right : Pore size distribution of cellulose acetate-based aerogels determined by mercury porosimetry

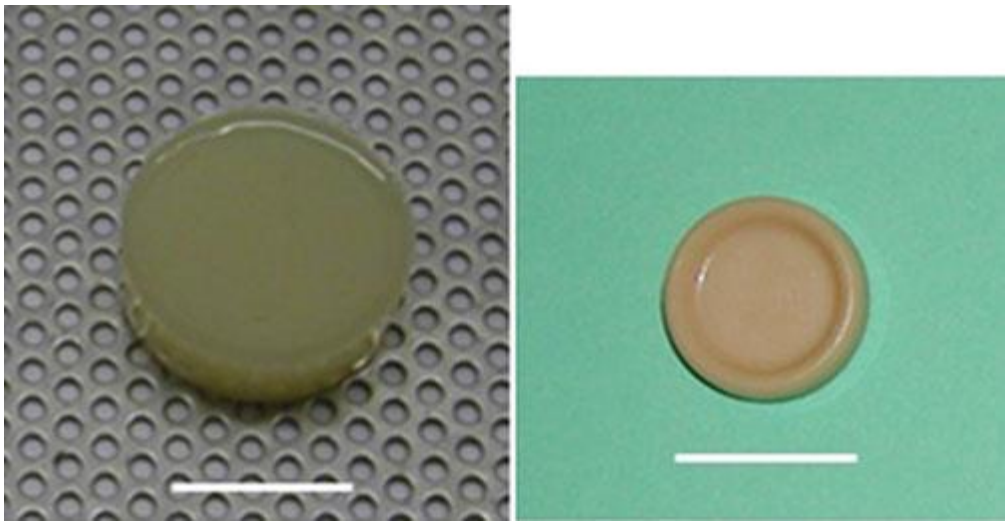


Figure 2 **source [1]**

Illustration of the shrinkage of cellulose acetate-based gels occurring during supercritical drying.

A wet gel (left) and the corresponding aerogel (right). The white bar is 2 cm-long

Figure 3 **source [1]**

Illustration of the shrinkage of cellulose acetate-based gels occurring during drying by evaporation.

A wet gel (left) and the corresponding xerogel (right). Even if the gel is slightly deformed it kept its structural integrity.

The initial diameter of the wet gel is 3 cm

Carbonization of cellulose aerogel leads to carbon aerogel, during this step the fibers diameter and length diminishes significantly [9]

Figure 4 source [1]

carbon aerogels obtained from pyrolysis of cellulose aerogels

I.2 Possible added properties

Hydrophilic aerogel can become hydrophobic by vapor deposition, the usual vapor compound being silanes [2]

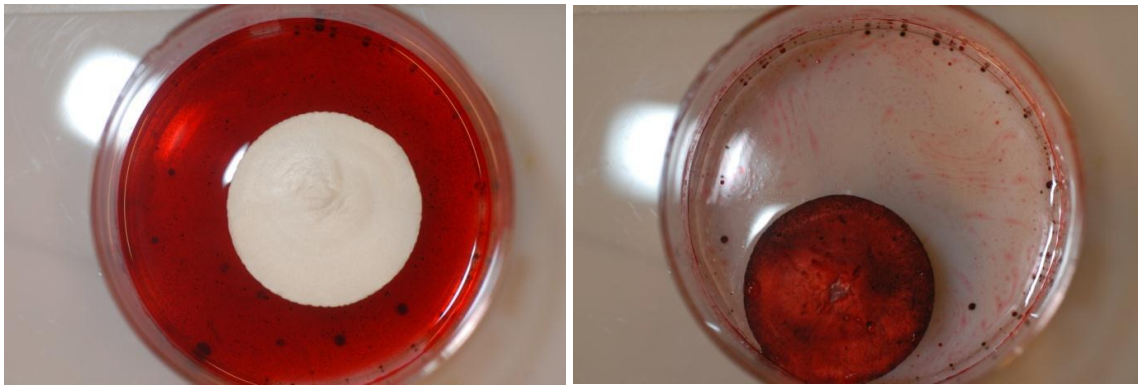


Figure 5 **source [2]**

A hydrophobic aerogel is able to float on water and simultaneously absorb a non-polar liquid (hexadecane, colored red) distributed on top of the water phase. The aerogel used in these experiments had been prepared from a 1 wt% NFC dispersion and it could be removed after the absorption without losing its integrity.

Due to their large open structure aerogel can be loaded with many materials either chemicals or nanoparticles [1]

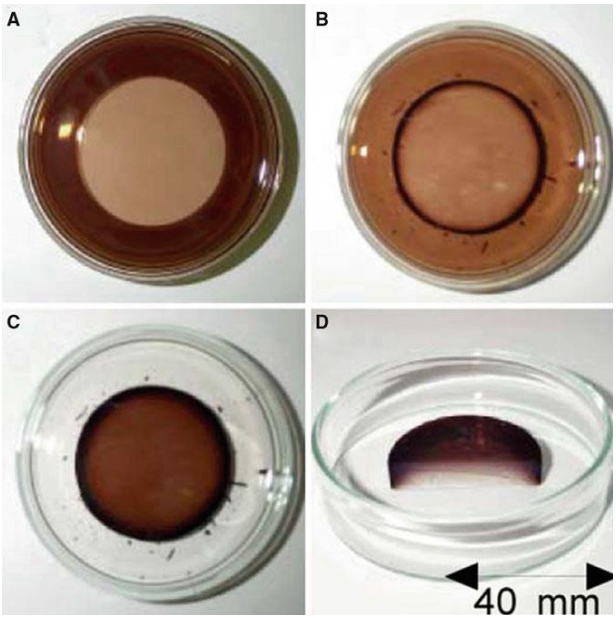


Figure 6 **source [1]**

Photographs of a silica wet gel immersed in a colloidal suspension of gold nanoparticles at

increasing times A–C. and of the Au–SiO2 composite aerogel D

II. Engineering an aerogel into a precise nanostructured template

II .1 existing deep ion beam lithography systems (IBL)

Focused ion etching is a common method to obtain nanostructures with good aspect ratio; penetration can be much higher than electron beam due to the bigger mass of the ions.

Aerogel due to their ultralow density are much easily penetrated by energetic beam than bulk materials for example a 40 kv electronic beam can go well beyond 1 mm deep into a silica aerogel and only 40 µm into bulk silica [3].

Complex multiple ion lithographic system can count more than 40 000 simultaneous 12.5 nm beams

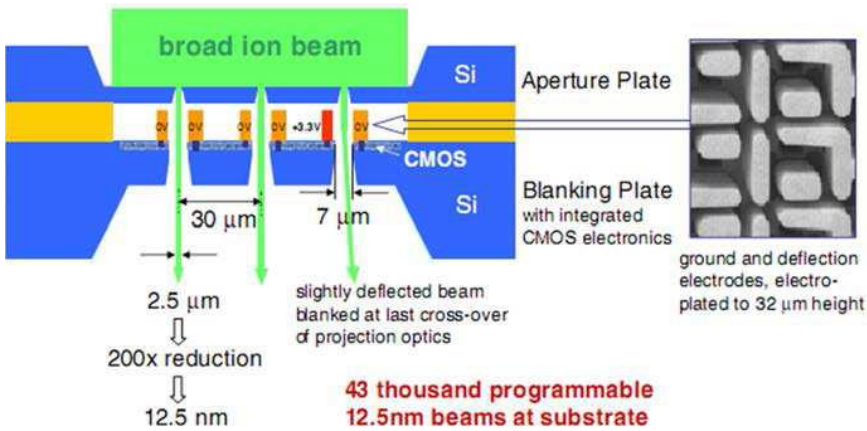


Figure 7 [source 4]

Schematics of a 43k-APS unit of the IMS system providing 43 thousand programmable beams

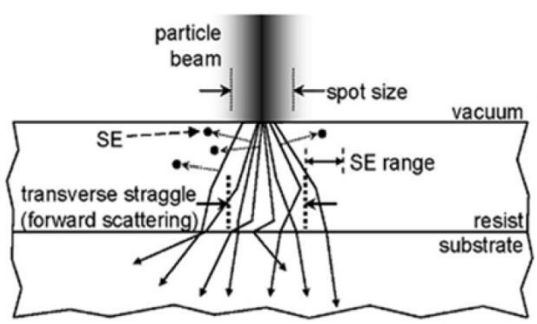


Figure 8 **[source 4]**

Factors limiting resolution of IBL. A focused ion beam irradiates a resist layer on a substrate. The three factors limiting resolution are (i) spot size of the beam (ii) ion scattering and (iii) secondary electron emission.

II.2 Proposed IBL system for local modifications on a hydrophobic cellulose aerogel

A massively (for example 200 000 X 200 000 matrix) IBL system can be built if the beam are simply non programmable straight lines (°, penetration of several cm may be possible for beams with energy in the range of 100-1000 Kev.

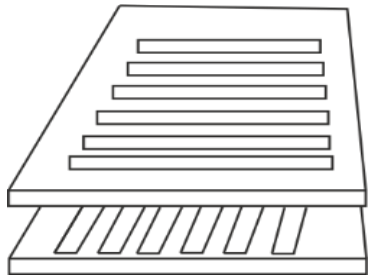


Figure 9

For example a simple matrix point grid can be done with two line grids on top of another at a 90° angle

On the other hand it is well know that hydrophobic materials having methyl groups can be turned hydrophilic with ozone which can be created by local energetic beams [5][6]

So it is proposed to create hydrophilic channels in a hydrophobic cellulose aerogel coated with surface methyl groups by bombardment of energetic O^{2-} ions.

Cellulose fiber are quite thick (10-15 nm) and the methyl groups are just in surface so a careful dosage should be able to "burn" only a few angstrom of each fiber and not compromise the aerogel structure

Figure 10

A hydrophobic cellulose aerogel (brown) is bombarded with focused beams of o2- ions (pink), creating hydrophilic channels

II.3 Making nanometric hollow tubes by capillary shrinking and oxidation

Even if the broadening of the channel in comparison of the ion beam diameter is expected to be much less marked than for bulk material due to the low density of the aerogel, obtained channels and natural pores are still too large to accurately maintain nanoparticles aligned within the set limits of the challenge.

One way to achieve this is to exploit the typical shrinking behavior of aerogel under capillary action at our advantage.

So one solution could be to drop water in order to fill the channels and then evaporate it very carefully in order to obtain a quasi-two-dimensional shrinking

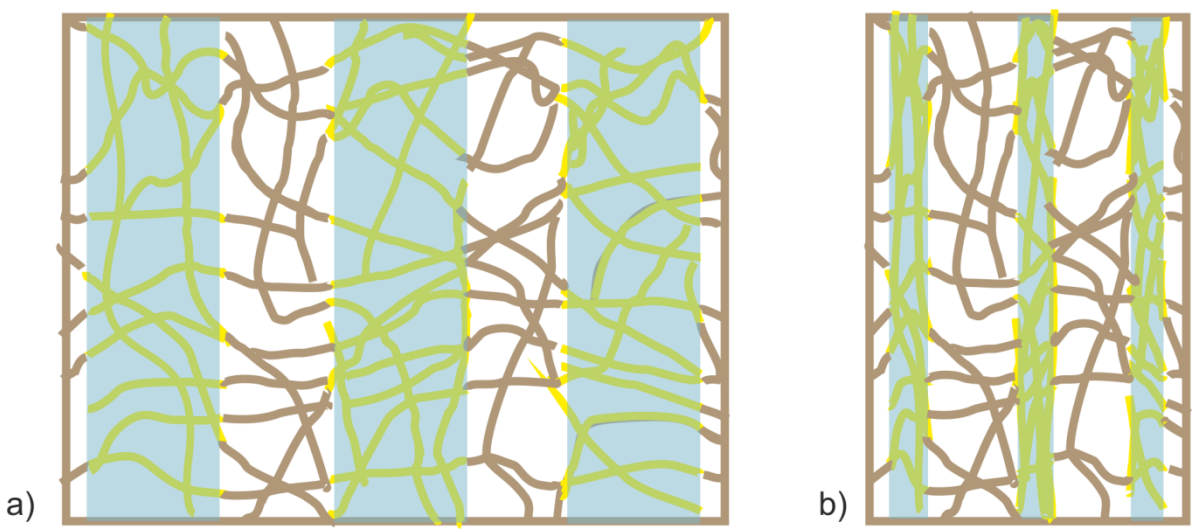


Figure 10

a) Water (blue) is dropped and the hydrophilic channel are filled

b) Due to the local filling and the high diameter to height ratio of the water channels a careful evaporation should lead to a quasi 2 dimensional shrinking leaving the hydrophobic zone with a low density

The main problem with this approach is that, due to the fiber non negligible diameter, the channel will rapidly stop shrinking and also become clogged preventing further filling with nanoparticles

II.3.1 Using hydrogen peroxide solution instead of pure water

Hydrogen peroxide solution is a very powerful oxidant that can burn cellulose completely [7].

This material has interesting properties for this challenge:

- Its oxidizing power can be modulated by temperature and concentration and is quite slow without catalysts permitting an easy control on the reaction
- Concentrated solutions can stay liquid even at very low temperature (up to -60°c)
- It can burn in solution a wide range of organic materials
- A diluted solution can be concentrated by evaporation because water have higher vapor pressure
- Its evaporation leaves no residues

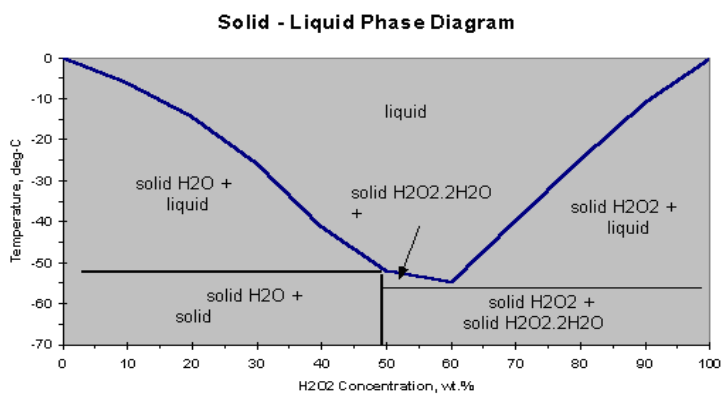


Figure 11 Solid-Liquid Phase Diagram **source [8]**

Concentration H_2O_2 at 25 °C [mass. %]	
Vapor	**Liquid**
1,9	32,1
8,0	55,7
24,1	73,8
35,0	77,8
58,4	88,3

Figure 10 **source [9]**

The equilibrium concentration of vapor and liquid phase of H2O2 reached by

Evaporation

II.3.2 Making hydrophilic nanometric hollow xerogel channels within an aerogel

By replacing pure water with a h2o2 solution it should be possible to burn precisely the fibers inside the tube in order to achieve the desired diameter, leaving a hollow xerogel tube with walls having little to no porosity.

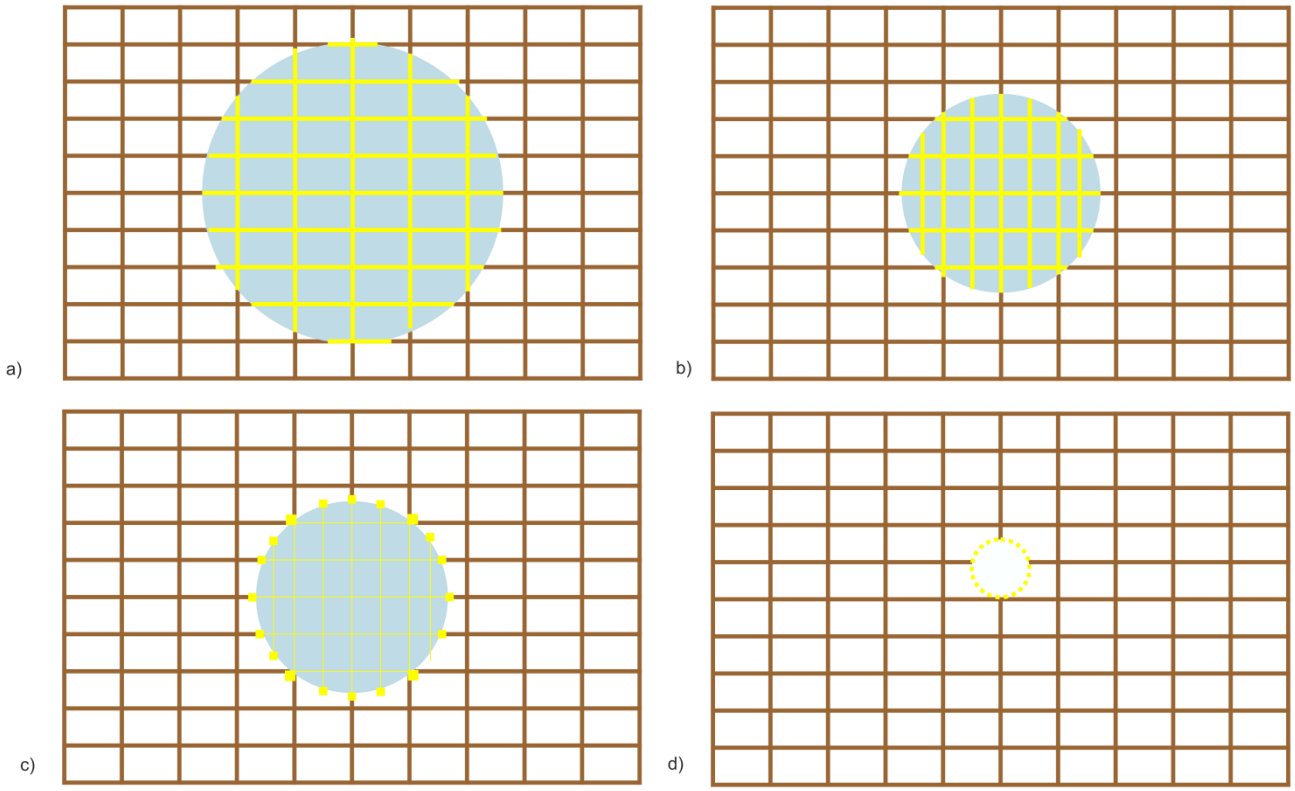


Figure 12

Top view of hydrophilic channels created into an aerogel

a. Filling the hydrophilic channel (yellow) with h2o2 solution (blue) in non oxidizing conditions
b. evaporate the solution in non oxidizing conditions until inner fiber density stop the collapse
c.) activate the oxidizing conditions and resume evaporation
d. when all the solution is removed a nanometric hollow xerogel tube is created (final step can be done with freeze drying to avoid total collapse), its walls are still hydrophilic and have very dense pore network than can retain nanoparticles

III Using the engineered aerogel as template for nanostructured objects

The following propositions are only quick examples and are by no means the only or best routes to achieve dense nanostructured objects

III.1 wet-dry approach

Nanoparticles of type 1 in solution are introduced in the hydrophilic channel either at the beginning of the shrinking /oxidation process or after the xerogel tubes are formed.

Filling can be improved using electric field, particles will migrate due to electrophoretic forces.

After evaporation the nanoparticles are constrained into a tube having a similar diameter forcing them to align.

Then the type 2 material is added using chemical vapor deposition (CVD).

Good densities should be possible as a similar technique is used to make carbon aircraft brakes [10].

The piece is then carbonized without oxygen to shrink the cellulose fibers diameter and open up new pores and to fuse the nanoparticles.

Once the material is porous again a high temperature treatment is done in an oxidative atmosphere to remove the carbon aerogel template.

Another chemical vapor deposition step is done to fill the open voids left by the burnt cellulose.

Then a final high temperature treatment is applied to achieve densification

III.2 wet-wet-dry approach

Nanoparticles of type 1 in solution are introduced in the hydrophilic channel either at the beginning of the shrinking /oxidation process or after the xerogel tubes are formed.

Then nanoparticles of type II in solution into a non-polar solvent are loaded into the non-hydrophilic zones of the aerogel

Filling can be improved using electric field, particles will migrate due to electrophoretic forces.

After evaporation, the type 1 hydrophilic nanoparticles are constrained into a tube having a similar diameter forcing them to align and the type 2 particles should form a more open network than with CVD

The piece is then carbonized without oxygen to shrink the cellulose fibers diameter to open up new pores and to fuse the nanoparticles.

Once the material is porous again a high temperature treatment is done in an oxidative atmosphere to remove the carbon aerogel template.

Another chemical vapor deposition step is done to fill the open voids left by the burnt cellulose.

Then a final high temperature treatment is applied to achieve densification

Conclusion

A method to make nanostructured materials using engineered aerogel template with hydrophilic channels was presented.

The ability of the aerogel to shrink upon drying was proposed as a way to attain nanometric dimensions.

Cellulose was the material chosen because of the relative abundance of data but other organic aerogels might be more suitable for this challenge.

For the same reason methyl silane hydrophobic coating was described even if it exists full organic hydrophobic coating that leave no residues on burning.

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Manuscript

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Adam R. Abate,‡a Julian Thiele,‡ab Marie Weinhartc and David A. Weitz*a

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3: DECOMPOSITION OF TISSUE PAPER

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Master of Science Thesis in Materials and Nanotechnology

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