

Around 200 mg of sample was dissolved in 2 mL of 40 % aqueous HF solution for the sodium chemical analysis by atomic absorption using the standard addition method.

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## Preparation of Titania Foams\*\*

By Arnout Imhof and David J. Pine\*

Porous materials find wide application as sorption media, lightweight structural materials, filters, insulators, and catalysts. The microstructure of porous materials determines their usefulness but can be difficult to control, especially for inorganic materials. In order better to control the microstructure, we recently developed a technique in which an emulsion was used as a template to make materials with uniform macropores using a sol-gel process.<sup>[1,2]</sup> In that process partially hydrolyzed alkoxides were allowed to form a monolithic gel in the liquid *outside* the emulsion droplets, thus forming a solid "cast" of the droplet phase of the emulsion. In this report we describe how the liquid alkoxides can also be emulsified *inside* the droplets. This leads to the formation of porous materials with a very different and interesting structure consisting of densely packed spherical shells.

To facilitate the sol-gel processing of water-sensitive alkoxides we use non-aqueous emulsions, that is, emulsions in which the water phase is replaced by another polar liquid.<sup>[3]</sup> Many apolar liquids can be emulsified as droplets in forma-

tion using certain triblock copolymers of ethylene oxide and propylene oxide as the surfactant.<sup>[3]</sup> The droplet phase can be any apolar liquid used in the more conventional aqueous emulsions. The key point for this communication is that the liquid alkoxides can be emulsified *inside* the droplets because of their apolar nature. These water-sensitive alkoxides are then protected from hydrolysis by the total absence of water. Hydrolysis and gelation occur only when the emulsion is exposed to water, producing a foam of spherical shells.

Several other methods are known to produce ceramics with a cellular or foam microstructure. Examples of such procedures are the selective removal of one component from a composite by leaching<sup>[4]</sup> or firing.<sup>[5]</sup> These methods produce materials with irregularly shaped pores, which are interconnected. They usually have a limited porosity. Foaming of sol-gel solutions<sup>[6]</sup> produces spherical pores and high porosities like the method described in this communication, but typically with much larger pores (>10  $\mu\text{m}$ ). Small (but also large) spherical pores can also be introduced by sintering of hollow ceramic beads.<sup>[7,8]</sup> The latter technique has the added advantage that the pore size distribution can often be kept narrow, whereas our method in its present form yields a broad distribution. Advantages of our technique are that the ceramic precursor solution is easily prepared and is stable indefinitely, even when a highly reactive precursor is used. Furthermore, it leads to materials with extremely high porosities. Yet, the macropores do not seem to be interconnected.

In this work we make titania foams using titanium tetraisopropoxide (TTIP, Aldrich, 97 %) as the alkoxide. Formamide (FA, Aldrich, >99 %, dried on molecular sieves 3A) was used as the polar liquid. The surfactant was the triblock copolymer (ethylene glycol)<sub>20</sub>-(propylene glycol)<sub>70</sub>-(ethylene glycol)<sub>20</sub>, obtained from Aldrich. Its molecular weight is 5800 and it contains 30 % by weight of ethylene glycol monomer. A solution of 1.75 % by weight of the surfactant in FA served as the polar phase. The apolar, or oil, phase was a mixture of 25 % by volume of titanium tetraisopropoxide, 74 % isooctane (2,2,4-trimethylpentane, Aldrich, 99 %), and 1 % silicon oil (Fisher, boiling point >200 °C, density = 0.959 g/mL). Equal volumes of the two solutions were mixed in a nitrogen atmosphere and agitated until a viscous emulsion was formed. The emulsion was poured into plastic cups and exposed to the atmosphere. Immediately, a skin began to form on the surface due to the diffusion of atmospheric moisture into the formamide and the subsequent hydrolysis of TTIP residing in the droplets. The atmospheric moisture was not controlled or measured. As the skin grew thicker the reaction slowed down. Water has a higher density than the emulsion so it could not be added from the top without disrupting the formation of the gel. Instead, more water was supplied by placing a filter paper moistened with a few drops of water over the gel and keeping the paper moist by adding some more drops every hour. Another strategy was to introduce about 1 mL of water be-

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low 5 mL of emulsion with a pipette. Substrates can also be dip coated and then exposed to moist air to form porous coatings. These had thicknesses in the range 0.1–1 mm. We found no influence of these different ways of preparation on the microstructure or the properties of the resulting porous material. After several days the stiff white gels were immersed in water for several hours, then decanted, and allowed to dry at room temperature. This yielded white pellets, which had typically shrunk by 20–25 % linearly.

A scanning electron micrograph (JEOL 6300F) of a dried gel is shown in Figure 1, revealing a structure that resembles a pile of egg shells. The material consists of a packing of thin spherical shells of many different sizes that are fused together. Many of the shells are broken at the side facing the viewer, but this is presumably the result of the fact that the sample was cut in order to observe the structure inside. Remarkably, the shells are very smooth and preserve the spherical droplet shape well. The hydrolysis and condensation reactions, therefore, did not disrupt the droplet interfaces. This may have been the result of the fact that hydrolysis and gelation of TTIP by water is extremely rapid. We suspect that immediately upon contact with water a solid skin is formed on the droplet surface, which prevents deformation and grows further by diffusion of TTIP from the inside of the droplet to the surface. In this way larger droplets form thicker shells than smaller droplets, as can be seen in Figure 1.

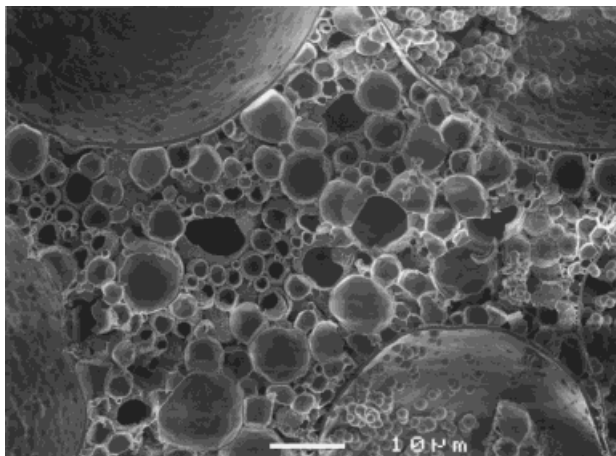


Fig. 1. SEM image of a titania foam made by the addition of water to a non-aqueous emulsion of titanium isopropoxide and iso-octane.

The thickness,  $d$ , of the shells can be estimated by assuming that the titania shell forms at the surface of a droplet with radius  $R$  and grows inward. Then Equation 1 can be derived.

$$\left(1 - \frac{d}{R}\right)^3 = 1 - f \frac{\rho_{\text{TTIP}} M_{\text{titania}}}{\rho_{\text{titania}} M_{\text{TTIP}}} \quad (1)$$

Here,  $f$  is the volume fraction of alkoxide in the oil,  $\rho$  the mass density, and  $M$  the molecular mass. Taking  $f = 0.25$

and assuming a density of  $2 \text{ g/cm}^3$  for the (uncalcined) titania gel we arrive at  $d/R = 0.012$ . This means that even a large droplet of  $10 \text{ }\mu\text{m}$  radius forms a shell of only  $0.12 \text{ }\mu\text{m}$  thickness. Close inspection of the larger shells in Figure 1 shows that this is a good estimate. Even shells less than  $1 \text{ }\mu\text{m}$  in size are seen to exist, even though they should be no more than a few nanometers thick.

The larger shells are also seen to contain some grainy material, which has the form of fused globules. Apparently, in the large shells some of the TTIP reacts with water inside the droplets and not just at the surface. It is unclear how this material is formed. Possibly, the droplet interfaces become less stable due to the reaction, which consumes part of the oil droplet and replaces it with titania and isopropanol. The volume changes involved and the miscibility of isopropanol with the continuous phase would lead to liquid flow, which could carry some of the continuous phase into the droplets. Considering all these processes it is remarkable that the overall droplet shapes are conserved quite well.

It is possible to convert the amorphous titania foams into crystalline  $\text{TiO}_2$  without collapse of the shells. Samples were heated in a furnace for 2 h in air at different temperatures with a heating rate of  $10 \text{ }^\circ\text{C/min}$ . The crystal structure was analyzed by powder X-ray diffraction using  $\text{Cu K}\alpha$  radiation (Philips X'pert-MPD). Scanning electron microscopy (SEM) images of titania foams calcined at  $800$  and  $1000 \text{ }^\circ\text{C}$  are shown in Figure 2. Note that the shell structure is completely preserved in both samples. However, the  $800 \text{ }^\circ\text{C}$  sample (top) consists of very smooth shells, whereas those in the  $1000 \text{ }^\circ\text{C}$  sample have become rough due to grain growth. The X-ray diffraction patterns in Figure 3 show that the titania has crystallized into the anatase structure after heat treatment at  $600$  and  $800 \text{ }^\circ\text{C}$ . The foam calcined at  $1000 \text{ }^\circ\text{C}$  has largely recrystallized to rutile, but there remains about 15 % anatase.

After calcination at  $600 \text{ }^\circ\text{C}$  the foams had shrunk by 40 % compared to their wet size. Their mass density was only  $0.16 \text{ g/cm}^3$ . If a density of  $3.84 \text{ g/cm}^3$  is assumed for anatase, this low density implies a very high porosity of 96 %. A similarly high porosity was found for titania foams calcined at  $1000 \text{ }^\circ\text{C}$ , which consisted largely of rutile (see Table 1).

Titania foams can also be made at a higher volume fraction of droplets. We made emulsions containing an oil volume fraction of 75 %. The oil had the same composition as before. The resulting foams again consisted of thin shells, but they were packed much more closely than the foams from the 50 % emulsions, as can be seen in Figure 4. A mass density of  $0.25 \text{ g/cm}^3$  was found for these foams, corresponding to a porosity of 93 %.

Nitrogen sorption isotherms were measured at 77 K on samples made from 50 % and 75 % emulsions and calcined at different temperatures (Micromeritics ASAP2000). The isotherms were of type IV, indicating the presence of mesopores. Most of the nitrogen was adsorbed in pores with a

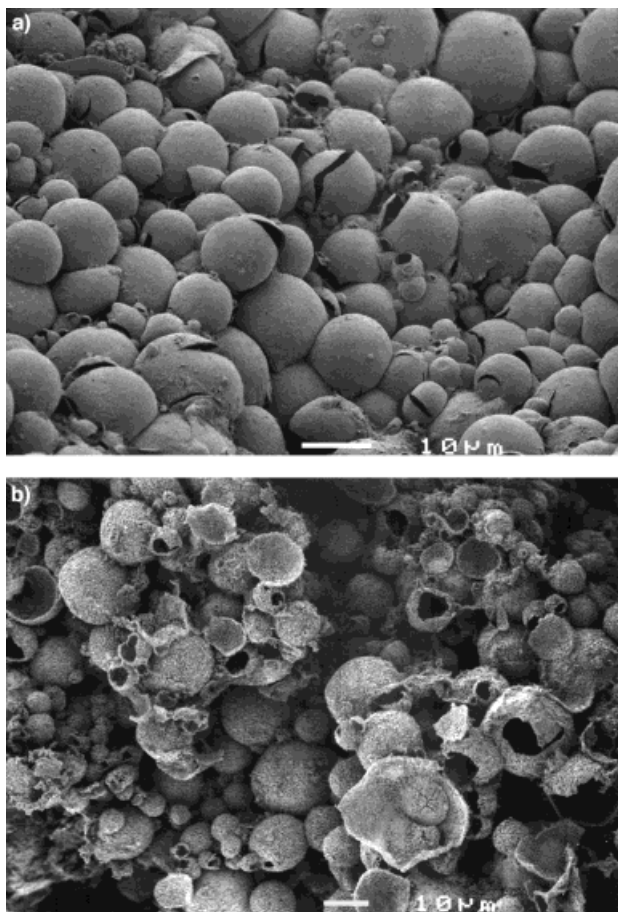


Fig. 2. SEM images of calcined titania foams. Top: Calcined at 800 °C, consisting of anatase. Bottom: Calcined at 1000 °C, consisting of 85 % rutile and 15 % anatase.

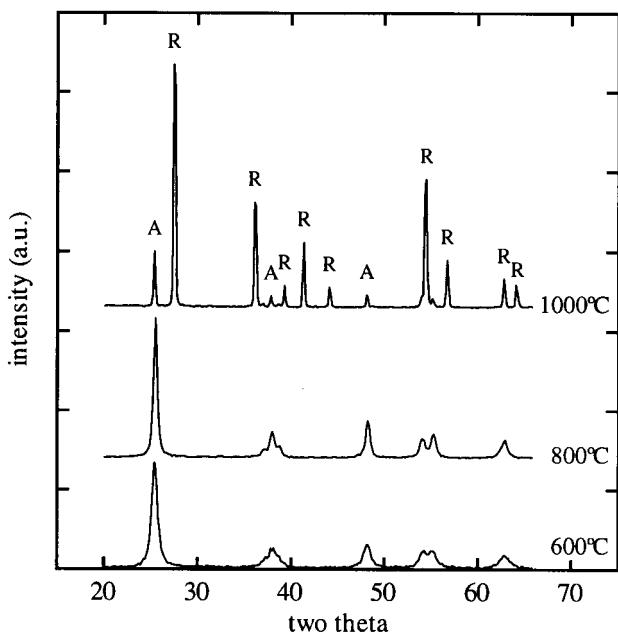


Fig. 3. Powder X-ray diffraction results of the titania foams calcined at different temperatures for 2 h, as indicated. The letters A and R are used to label the peaks corresponding to anatase and rutile, respectively.

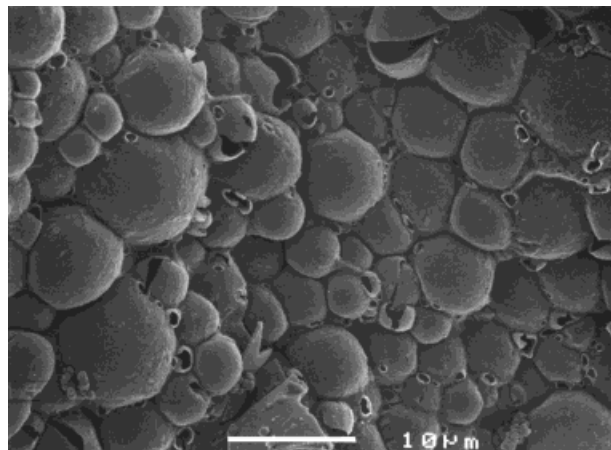


Fig. 4. SEM image of a titania foam made from an emulsion with 75 % v/v TTIP and isooctane, and 25 % v/v formamide.

diameter smaller than 10 nm. The BET (Brunauer–Emmett–Teller) specific surface areas are given in Table 1. These data indicate that the titania shells are mesoporous, as are all structures formed through sol-gel processes. The mesopores also provide a pathway by which liquid could be removed from the foams during the drying stage without bursting the shells.

Table 1. BET specific surface areas  $S_{\text{BET}}$  and porosities of the titania foams after calcination.

Amount of oil	Property	Calcining temperature		
		600 °C	800 °C	1000 °C
50 %	$S_{\text{BET}}$ [m <sup>2</sup> /g]	94	20	8.4
	Porosity [%]	96	96	95
75 %	$S_{\text{BET}}$ [m <sup>2</sup> /g]	65	11	~1
	Porosity [%]	93	94	93

The mesoporosity of the titania shells can be reduced by heating with little effect on the macroporosity. The numbers in Table 1 show that the specific surface area of the titania foams drops rapidly at higher calcination temperatures. This is due to the removal of micro- and mesopores, which provide most of the internal surface area measured from the BET analysis. The total porosity is hardly affected, however, because the total porosity is determined mainly by the macropores (formed by the shells). The macropores contribute little to the surface area because of their relatively small surface-to-volume ratio. This means that the total porosity can be set by the composition of the emulsion, but that the specific surface area can be influenced using the calcination temperature.

In summary, water-sensitive metal alkoxides can be emulsified in formamide. When these non-aqueous emulsions are exposed to water, hydrolysis and gelation of the alkoxide give rise to interesting and potentially useful macroporous materials. In this way we made highly porous titania with a microstructure consisting of very thin spherical shells. The structure is very robust and is conserved



even when the titania is converted to its crystalline forms anatase and rutile by calcination.

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## Dendrimer-Based Self-Assembled Monolayers as Resists for Scanning Probe Lithography\*\*

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The feature sizes of microelectronic circuitry components fabricated by current photolithographic processes are ultimately limited by the wavelength of the exposing radiation used for photochemical transformations. In the pursuit to develop faster and smaller semiconductor devices, both new materials and lithographic processes for nanofabrication are currently under exploration by industry and academia alike. The highest possible resolution is of the order of the size of the individual pixels that compose the image. Therefore, to obtain patterns with nanometer scale resolution, a lithographic process should manipulate materials made from molecules with dimensions no larger than the desired pixel size.

We are currently exploring the use of dendrimer-based monolayers as resists for scanning probe lithography (SPL). The well-characterized globular and monodisperse properties of dendrimers make them ideally suited for self-assembly on a surface.<sup>[1-4]</sup> Due to their compact size, the ultra-thin films formed from dendrimers have a thickness much less than can be obtained by spin-coating ordinary linear polymers. In addition, we have observed that the dendritic monolayers are more stable than the analogous monolayers consisting of low molecular weight alkylsilanes. This may be due, in part, to the polymeric and dense nature of dendrimers, resulting in better protection of the anchoring group.

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The scanning probe microscope (SPM) has recently been shown to be a versatile tool for nanolithography. The SPM may be used for the anodization of passivated metal surfaces,<sup>[5-12]</sup> or it can act as a low energy electron source for patterning organic polymer thin films.<sup>[13-16]</sup> The scanning probe has also been used to pattern both organosilane<sup>[17]</sup> and alkanethiolate<sup>[18]</sup> monolayers on silicon and gold, respectively. We have been investigating the possibility of using ultra-thin polymeric films, such as dendrimer monolayers, as resists for SPL. Such resists might be attractive for SPL since a post-exposure wet development step would not be required prior to etching.

We have investigated the properties of monolayers and ultra-thin films formed from poly(benzylether) dendrimers,<sup>[19,20]</sup> terminated with both benzyl and *tert*-butyldiphenylsilyl ether groups (Fig. 1), because of their relative ease of preparation and derivatization. We report here our studies on dendritic monolayer formation via covalent attachment to a silicon substrate and the lithographic patterning of these monolayers using SPL.

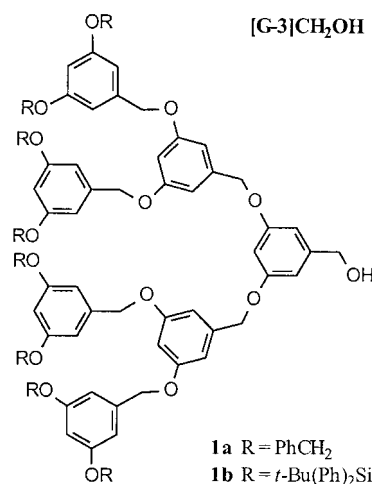


Fig. 1. Structures of two poly(benzylether) dendrimers, terminated with both benzyl and *tert*-butyldiphenylsilyl ether groups.

Both the benzyl ether terminated dendrons<sup>[20]</sup> (**1a**) and the silyl ether terminated dendrons<sup>[21]</sup> (**1b**) were prepared according to previously reported procedures. For the covalent attachment to the silicon wafer surface, the benzylic alcohol functionality of the dendrons was first acylated with 10-undecenoyl chloride to give esters **2a,b** (Scheme 1). Platinum-catalyzed hydrosilylation of the terminal olefin with either mono- or tri-chlorosilanes using Karstedt's catalyst afforded the corresponding chlorosilanes **3a-d** in quantitative yields. Polished, n-type Si(100) wafers were cleaned and surface oxidized prior to use by immersion in a piranha bath for 30 min at 120 °C. The self-assembled monolayers were prepared by immersing the wafers in a solution of the appropriate silyl chloride (5 mM) in freshly distilled toluene for 48 h.

The covalently bound dendrimer monolayers (Fig. 2) were characterized by contact angle goniometry using the