

MACROPOROUS MATERIALS WITH UNIFORM PORES BY EMULSION TEMPLATING

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ABSTRACT

A method was developed for the production of macroporous oxide materials by using the droplets of a nonaqueous emulsion as the templates around which material is deposited through a sol-gel process. Moreover, uniform pores arranged in regular arrays can be obtained by starting with an emulsion of uniform droplets. These droplets first self-assemble into a colloidal crystal after which gelation of the suspending sol-gel mixture captures the ordered structure. After drying and calcination pellets are obtained which contain ordered arrays of spherical pores left behind by the emulsion droplets. The method can be used to make uniform pores in the range from 0.05-5 micrometers in many different materials. We demonstrate the process for titania, silica, and zirconia.

INTRODUCTION

There is intense interest in producing porous materials with highly uniform pore sizes for use as catalytic materials, filters, and adsorbents. Methods exist for the fabrication of materials with uniform pores of diameter less than ca. 20 nm [1,2]. They are formed by templating surfactant molecules with inorganic solutes such as silicates. However, there is no general method for producing such materials with uniform pore sizes at larger length scales. Existing processes for producing macroporous materials result in a very broad distribution of pore sizes [3,4]. Here, we report a new method for producing macroporous materials with highly uniform pores in the size range from 50 nm to several micrometers. A consequence of the high uniformity of the pores is that they order into crystalline lattices. This could make these materials also useful in optical devices such as photonic band gap materials [5,6].

The basic strategy is to use the droplets in an emulsion as the inert templates for a sol-gel process that takes place in the continuous (external) phase of the emulsion. Emulsions of equally-sized droplets can be produced through a repeated fractionation procedure [7]. Such monodisperse droplets undergo a spontaneous transition to an ordered colloidal crystalline phase [8]. The sol-gel process is then used to produce a space-filling gel of one of a range of possible solid materials. This gel encapsulates the droplets, thus forming 'imprints' of the them in the resulting material. The major advantage of templating emulsion droplets (as opposed to solid microparticles) is that the droplets can easily be removed by evaporation or dissolution *prior to* drying of the gel. Since drying is accompanied by significant shrinkage we found that this feature is essential in order to obtain uncracked materials. A further advantage is that the deformability of droplets allows emulsion volume fractions in excess of the close packing limit for hard spheres (74%). This enables the fabrication of porous materials with filling fractions lower than 26%. Such materials have a connected pore system.

One of the problems that has to be overcome to make this strategy work is that sol-gel processes in general make use of metal alkoxides dissolved in an alcohol and hydrolyzed by the controlled addition of water. Conventional emulsions, however, are aqueous systems and are thus incompatible with most metal alkoxides. We therefore first developed a suitable nonaqueous emulsion [9] in which the water is replaced by another polar liquid, namely formamide. This led to stable oil-in-formamide emulsions. Then, the sol-gel process was adapted so that it would work in the highly polar formamide as the solvent instead of the usual lower alcohols.

We demonstrate the emulsion templating process by making ordered macroporous titania, silica, and zirconia. It should, however, not be difficult to adapt the process to making a range of other metal oxides, binary metal oxides, and even organic polymer gels.

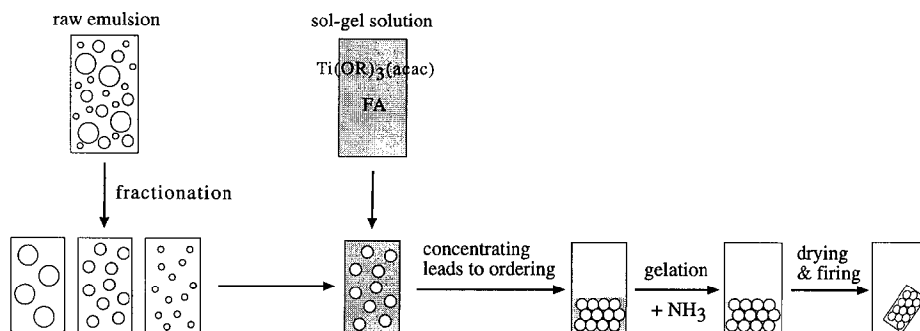


Figure I. Schematic of the emulsion templating process.

EXPERIMENT

The emulsion templating process is shown schematically in Figure I and is further detailed below.

Emulsion preparation

In ref. [9] it was found that stable nonaqueous emulsions can be prepared with formamide (FA) as the continuous phase. A surfactant that gives optimal stability was the symmetric triblock copolymer (ethylene glycol)₂₀-(propylene glycol)₇₀-(ethylene glycol)₂₀. Its molecular weight is 5800 and it contains 30% by weight ethylene glycol monomer. For the emulsion templating we used oil that consisted of 99% iso-octane and 1% silicone oil. The silicone oil (or another high molecular weight oil) is needed to prevent droplet coarsening due to Ostwald ripening [9].

In a typical recipe 20 g of surfactant was dissolved in 1 liter of formamide. Then 150 ml of oil was emulsified in it using a homogenizer. The emulsion was fractionated with the method described in ref. [7]. This resulted in a dozen or so monodisperse emulsions of between 1 and 3 ml in size, each having an oil volume fraction of about 50%.

Sol-gel precursor solution

A typical preparation is as follows: 26 mmol of titanium tetraisopropoxide (97%) was treated with an equimolar amount of the chelating agent acetylacetonate (acac) to reduce its reactivity with water. The resulting complex is insoluble in formamide but it can be made soluble by partial hydrolysis at a H₂O/Ti ratio of between 3 and 10. Thus, the solution was mixed by vigorous stirring with a mixture of 1.6 g of water in 6.6 g of formamide. The resulting clear yellow solution contains a considerable amount of isopropanol produced by the hydrolysis reaction. Since isopropanol will destabilize the emulsion, it was removed by extracting twice with a fivefold excess of hexanes. The resulting yellow liquid was frequently turbid. Briefly heating it to ~90°C produced a clear yellow and slightly viscous solution. Its color changed slowly from yellow to orange over the course of a few days but it did not form a precipitate for several weeks. The solution was used for templating within a few days. We found that it forms a clear rigid gel a few hours after mixing it with a small amount of 30% ammonia.

A sol-gel solution for zirconia was made in the same way, starting with a 70% zirconium tetra-*n*-butoxide solution in *n*-butanol. A silica precursor solution was made by mixing 4 ml of silicon tetramethoxide into a mixture of 1 ml 0.1 M HCl and 5 ml formamide, and the hexane extraction was not used.

Emulsion templating

The emulsion droplets were then transferred to the sol-gel solution. First, 2 wt% of the surfactant

was dissolved in the sol-gel solution for droplet stabilization. Then, 1 ml of a 50% v/v emulsion of monodisperse droplets was mixed with 3 ml of the sol-gel solution. The droplets were centrifuged at 1500 rpm and collected as a cream. This was then redispersed in another 3 ml of the sol-gel solution, and centrifuged again. The resulting concentrated emulsion was transferred to a polyethylene vial and mixed with a tiny amount of 30% ammonia from a syringe such that the molar ratio $\text{NH}_3/\text{Ti} \approx 1$. This induced gelation in about 3 hours, which is enough time for the droplets to self-assemble into a crystalline lattice whenever the droplets take up more than ~50% of the final emulsion volume [8]. About 16 hours after gelation the gel was aged at 50°C for 24 hours. Then it was immersed in plenty of ethanol for 24 hours in order to extract formamide, isooctane, and surfactant, all of which are all soluble in ethanol. The gel was then dried slowly at room temperature over several days and finally calcined in air in a furnace at temperatures of up to 1000°C for 2 hours with a heating rate of 15°C/min.

Analyses

The porous materials were examined with a JEOL 6300F Scanning Electron Microscope (SEM). Samples were prepared by breaking a small chip off the pellets and polishing the exposed, internal surface with diamond paper and sputtering it with gold. X-ray diffractograms were taken with a Philips X'pert-MPD using Cu-K α radiation. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP2000 on samples degassed at 200°C for 4 hours. Thermogravimetric analysis (TGA) was done with a Mettler TA3000 on gels dried at 60°C.

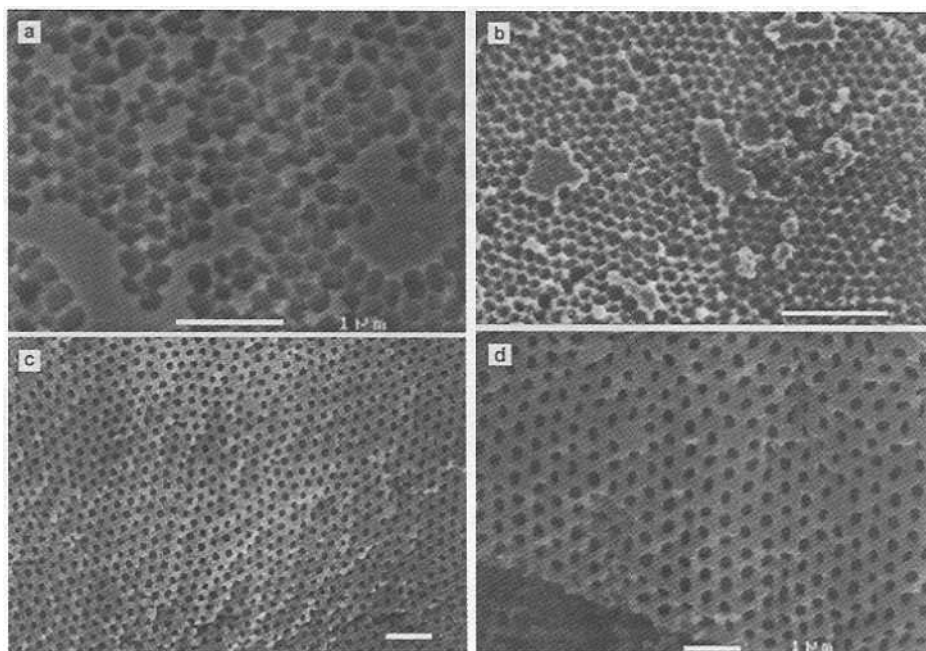


Figure II. SEM images of emulsion templated titania showing ordered macropores. *a*. After drying at 60°C; *b*. Same sample after calcination at 1000°C; *c*. Highly ordered sample calcined at 1000°C; *d*. Same as *c* showing an edge with cusps. Scale bars are 1 μm .

RESULTS

The emulsion templating procedure yielded white pellets that were usually uncracked. The whiteness is due to strong scattering of light by the macropores which are on the order of the wavelength of visible light.

A SEM picture of a dried (but not calcined) macroporous titania gel is shown in Figure IIa. The droplets have left behind uniform spherical pores of 175 nm that show ordering into hexagonal domains. The original emulsion had a droplet volume fraction of about 55%. During the drying process the gel shrunk to about 50% of its wet size. Thus, the templating process was successful. The pore structure did not collapse, even though drying generally produces very large stresses in the gel. This is due in large part to the fact that the template was removed *before* drying. It is possible that residual surfactant in the gels also helped to reduce the stresses by lowering the surface tension of the menisci that form during drying.

In order to remove residual organic material and to permit densification of the titania matrix most gels were given a heat treatment. In Figure IIb the same sample is shown as in Figure IIa after being calcined at 1000°C. The titania has become a little more 'grainy', but the ordered pore structure has remained completely intact. Due to the densification of the titania matrix the pores have shrunk to 145 nm but apparently these processes did not damage the pore structure.

Figure IIc shows a titania sample with a high degree of pore order. The pores appear not to be touching, but this is caused by the fact that the pores were 'decapitated' by the surface. Their actual diameter is closer to the average distance between pore centers (380 nm). This can be seen in the bottom left hand corner of Figure IId, where the edge cuts through the middle of the pores showing cusps corresponding to the size of the macropores. These images also show that the pore lattice exhibits normal lattice defects such as vacancies and dislocations.

A typical TGA trace of a titania gel is seen in Fig. III. These samples typically lost 30-35% of their weight during the heat treatment. Above 500°C weight loss is essentially complete. Most of the loss is probably due to the oxidation of unhydrolysed acetylacetonato groups and to evaporation of formamide which has a high boiling point of 210°C.

The densification of the TiO₂ matrix was further studied by measuring nitrogen sorption isotherms. The isotherms up to 800°C were of type IV and showed mesoporosity in the range 2-10 nm. At 900°C the isotherms changed to type II, which indicates that no pores smaller than ca. 50 nm exist. From the data the BET specific surface area (S_{BET}) of the titania samples was calculated as well as the total volume of pores smaller than 50 nm. Note that this 'mesoporosity'

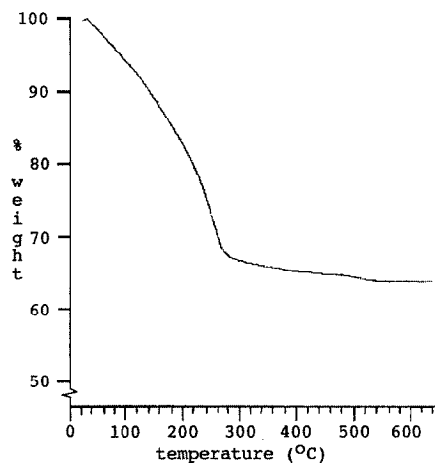


Figure III. Thermogravimetric analysis of a macroporous titania gel.

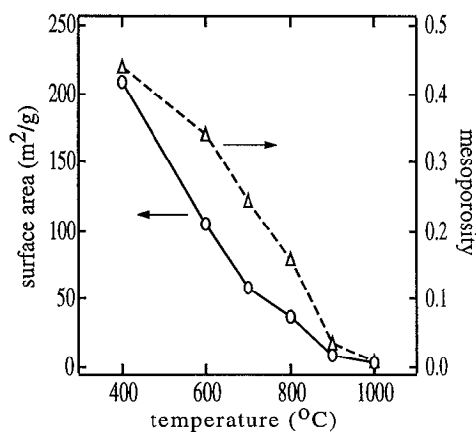


Figure IV. Specific surface area (circles) and mesoporosity (triangles) of macroporous titania.

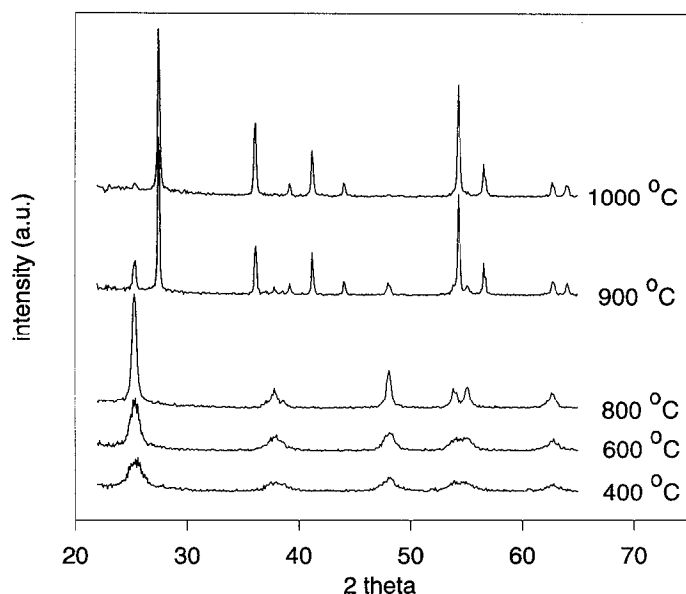


Figure V. X-ray powder diffraction of titania matrix after 2 hour heat treatment at the temperatures shown. The anatase structure changes to rutile at 900°C.

therefore does not include the volume of the macropores formed by the templating mechanism. The results are shown in Figure IV and show a strong densification of the TiO_2 matrix in the range 400-1000°C. This kind of control is useful because it can be done without harming the macropore structure. In applications such as in catalytic materials, for example, the macropores facilitate transport to mesoporous internal regions where reactions can take place.

The crystallinity of the TiO_2 matrix as a function of calcination temperature was investigated by X-ray diffraction; see Figure V. Diffraction maxima first appear at around 400°C and are quite broad, indicating very small TiO_2 crystallites. We calculated an average crystallite size of only 7 nm using the Scherrer formula. At higher temperatures the peaks sharpen due to grain growth. The diffraction pattern corresponds to TiO_2 in the anatase structure. At 900°C the titania recrystallized to rutile, but still contained some anatase. Above that temperature only rutile was present and the grains had grown to 60 nm. It was satisfying to see in SEM images, however, that all these microstructural changes affected only the matrix material but had no effect upon the ordered pore structure. Only at 1100°C did the pore structure begin to degrade as a result of excessive grain growth.

In order to demonstrate the versatility of the emulsion templating technique we also made ordered macroporous zirconia and silica. SEM images of these samples are shown in Figure VI. The silica sample had a high porosity of 89%. This was only possible due to deformation of the emulsion droplets in the original emulsion. As a result the voids in the gel overlap, thus creating a continuous pore structure.

CONCLUSIONS

Templating of nonaqueous emulsions is a new and versatile technique that allows one to fabricate macroporous materials with ordered pores. It is also inexpensive, yields uncracked materials, and

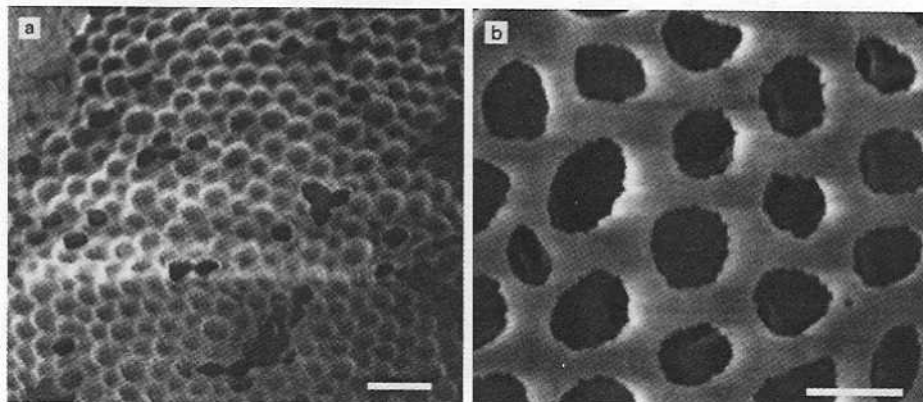


Figure VI. *a.* SEM image of emulsion templated ZrO₂ after calcination at 1000°C. *b.* SEM image of emulsion templated SiO₂ calcined at 600°C. Scale bars are 1 μm.

can be applied to a wide variety of solids. Of course, in applications where a uniform pore size is unimportant emulsion templating still has these advantages, but other methods exist. When size uniformity is desired, however, emulsion templating is the only method available to produce macroporous materials. The most severe limitation currently is the production of large quantities of monodisperse emulsion. The fractionation process that we have used thus far is time consuming and yields only small amounts of material. Thus, it would be desirable to develop a more efficient means for the production of large quantities of monodisperse emulsions. Developing schemes for producing highly ordered droplets in the emulsion prior to gelation is also a high priority. Promising routes include application of shear flow and external fields, and droplet deposition on surface microstructures [10,11].

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