

## Research News

# Uniform Macroporous Ceramics and Plastics by Emulsion Templating\*\*

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## 1. Introduction

Macroporous materials with uniform pore sizes in the range from 50 nm to 10  $\mu\text{m}$  are predicted to have unique and highly useful properties as optical devices, specifically for use as photonic crystals with optical bandgaps.<sup>[1]</sup> Moreover, the ability to control pore size and uniformity could produce improved filters, membrane supports, catalytic materials, and adsorbents. Nevertheless, until very recently, there has been no general method available for producing such materials. The primary problem has been controlling the pore size distribution; existing techniques result in an extremely broad distribution of pore sizes.<sup>[2]</sup> Moreover, the ability of existing techniques to control the overall porosity of macroporous materials is limited. The purpose of this article is to describe a new method for producing macroporous materials with highly uniform pores in the range from 50 nm to 10  $\mu\text{m}$ . The technique can also produce materials of any desired porosity up to approximately 90 %.

## 2. Background

Making materials uniformly structured on microscopically small scales requires a miniature template that directs the formation of the solid matrix. Modern techniques such as micromachining and photo- or X-ray lithography are available and are capable of making complicated structures down to feature sizes of less than a micrometer. However, these techniques are usually limited to two-dimensional surface structures. In principle, three-dimensional structures can be built up from the two-dimensional templates, but such processes are tedious, complicated, and generally incapable of producing more than a few layers into the third dimension. They are also expensive to implement on a large scale.

Using self-assembling microparticles provides an alternative route to making microstructures. Self-assembly has the

advantage of producing intrinsically three-dimensional structures and avoids the complicated techniques of micromachining and lithography, though the choice of structures is more restricted. For the length scales of interest here, from 0.1 to 10  $\mu\text{m}$ , the relevant self-assembling systems are colloidal suspensions. Monodisperse microspheres suspended in a liquid order spontaneously to form face-centered cubic (fcc) or body-centered cubic (bcc) crystals when sufficiently concentrated<sup>[3]</sup> or when electrically charged.<sup>[4]</sup> Binary mixtures of microspheres of appropriately chosen size ratios lead to other crystalline structures, such as the  $\text{AB}_{13}$  or  $\text{AB}_2$  cubic phases.<sup>[5]</sup> Elongated particles are known to spontaneously form phases with nematic or smectic order. All of these ordered colloidal phases represent microstructured materials themselves, but they also provide highly useful templates for other materials. A further advantage of colloidal suspensions is that intense research over the past several decades has taught us a great deal about how to manipulate and induce ordered structures. For example, shear flow,<sup>[6]</sup> electric fields,<sup>[7]</sup> and surface microstructures<sup>[8]</sup> can all be used to choose the desired kind of order and to reduce the number of defects.

When using colloidal particles as templates for making new materials, it is important to be able to remove the template after using it without disturbing the structure it supports. For this reason, we use *liquid* colloidal droplets, i.e., liquid droplets suspended in another insoluble liquid and stabilized by a surfactant (an emulsion). Liquid droplets are easily removed by dissolution or evaporation after templating and prior to further processing. This is extremely important since processing generally gives rise to considerable shrinkage (e.g., during drying), which can lead to cracking and pulverization. Such deleterious effects can be prevented if the template is removed first.

## 3. Emulsion Processing

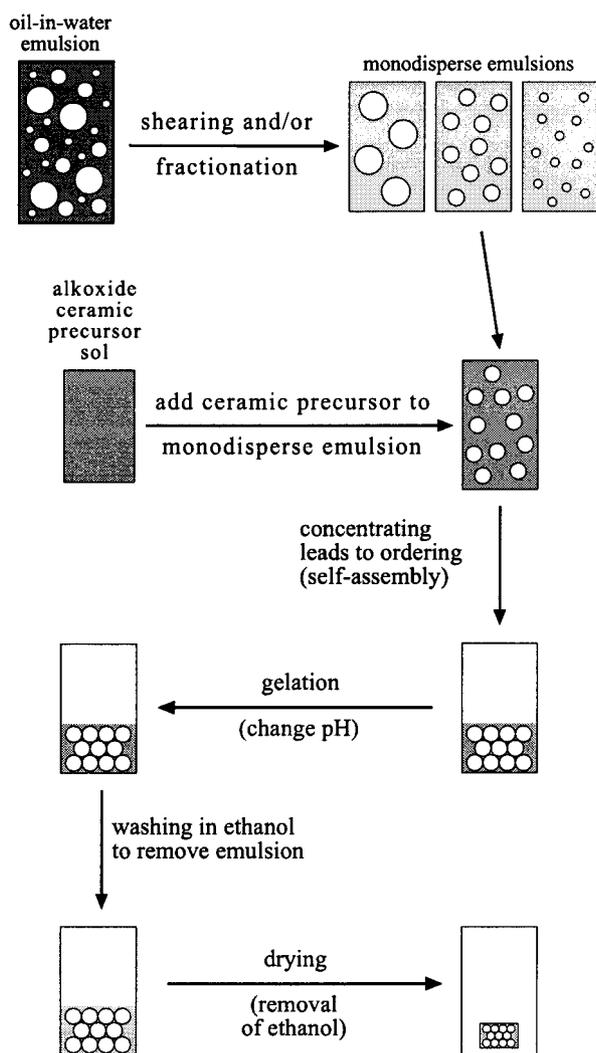
The basic idea of our method is to use a highly uniform dispersion of liquid emulsion droplets as a template around which solid material is grown. A variety of techniques is available for growing the solid material, including sol-gel chemistries as well as various polymerization techniques

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[\*\*] This material is based on work supported by the US Army Research Office under grant number DAAG55-97-1-0372.

for making organic materials. First we describe the emulsions and how they are produced, then the different ways in which they can be manipulated to form uniform, ordered structures. In the following sections, we describe different methods for growing the solid material. A schematic of the templating process is shown in Scheme 1.

Emulsions are droplets of one fluid dispersed in a second immiscible fluid and stabilized by a surfactant. Unlike microemulsions, which are thermodynamically stable phases and which form spontaneously, emulsions are metastable and are usually produced by mechanically induced droplet breakup. Thus, most emulsification schemes result in a distribution of droplet sizes. To obtain highly monodisperse



Scheme 1. Top row: Mechanical mixing produces polydisperse emulsion from which a monodisperse emulsion is made using shear flow and/or fractionation. Second row: Sol of ceramic precursor is added to the continuous (outer) phase of the monodisperse emulsion. Third row: Concentration of the emulsion by centrifugation leads to self-assembly of the droplets into a close-packed structure. The addition of ammonia increases the pH and induces gelation of the continuous phase. Bottom row: Liquid emulsion components and surfactant are replaced by alcohol by repeated washing of the gel. Subsequent drying, accompanied by shrinkage of up to 50 %, results in a solid porous material with the ordered structure of the concentrated emulsion preserved.

emulsion droplets, subsequent processing is usually necessary, though in certain special cases there exist methods for producing highly monodisperse emulsions in a single step. Thus, we usually generate emulsions mechanically and then use a recently developed fractionation procedure to produce monodisperse emulsions.<sup>[9]</sup> In this way, we typically obtain emulsions with a droplet polydispersity of about 10 %. With increased effort, emulsions with a polydispersity of a few per cent or less can be achieved. When the volume fraction of droplets is sufficiently high, typically above 50 %, monodisperse emulsion droplets spontaneously order to form a close-packed structure. The volume fraction of droplets can be continuously varied from essentially zero to in excess of 90 %.

The emulsion droplets can be further manipulated to alter the lattice or to reduce the number of lattice defects using techniques developed in colloid science. For example, while concentrated suspensions are known to form close-packed crystals, they may contain stacking faults. These may be removed by application of a shearing flow so as to obtain a perfect fcc lattice.<sup>[6]</sup> Electric fields have similar ordering effects on particle suspensions.<sup>[7]</sup> The droplets can also be allowed to settle onto a surface with microstructures made by lithography<sup>[8]</sup> or microcontact printing. This can be used to impose a desired lattice constant and symmetry on the droplet packing.

## 4. Gelation

The droplet structure can be permanently captured by gelation of the liquid in which the droplets are suspended.<sup>[10]</sup> The reaction producing the solid material thus results in a monolithic gel. Such gels can be made from organic materials using polymerization reactions or from inorganic materials using sol-gel chemistry.<sup>[11]</sup> Since these reactions are quite general, emulsion templating can be used to make porous structures in a wide range of materials. For each material the only requirement is that the precursor molecules be compatible with the components that make up the emulsion (e.g., they do not destabilize the emulsion).

A compatible emulsion can usually be found because a variety of liquids can be used to make emulsions. The only requirements are that the two liquids be mutually insoluble and that a suitable surfactant can be found to stabilize the droplets against breakup. Thus, the choice of liquids can be adapted to meet the requirements of the chemistry that is used to grow the solid phase around the droplets. In some cases, conventional oil-in-water emulsions (or inverse water-in-oil emulsions) can be used; in other cases, non-aqueous emulsions<sup>[12]</sup> may be required to accommodate the chemistry used to grow the solid matrix. In either case, the only role of the surfactant is to stabilize the emulsion; it need not be otherwise involved in the templating process.

After gelation the droplets are removed by evaporation or dissolution in a suitable liquid. The gel is now ready to be dried leading to the macroporous material. It may also be necessary to give inorganic materials a heat treatment to remove residual organic material from the sol-gel process. There may be a small amount of shrinkage during heating but since the template has already been removed, cracking does not occur.

## 5. Production of Uniform Macroporous Materials

Uniform macroporous silica is made in an aqueous emulsion of uniform iso-octane droplets stabilized by sodium dodecylsulfate (SDS). A suitable sol can be made by dissolving 3 mL of tetramethoxysilane in 9 mL of 0.01 M aqueous hydrochloric acid. Most of the methanol formed by hydrolysis of the alkoxide is distilled off at room temperature under a low vacuum. The uniform oil droplets, as a concentrated emulsion of ca. 2 mL, are then transferred to this sol simply by mixing. The emulsion is then centrifuged to increase the droplet volume fraction, which should be higher than 50 % to induce spontaneous ordering of the droplets. The emulsion thus obtained gels some time after adding a small amount of concentrated ammonia, or after it is exposed to an atmosphere containing ammonia. The white gel is aged and then washed extensively with ethanol to remove water, iso-octane, and SDS. The gel is then carefully dried and fired in a furnace at 600 °C in air to remove residual organic material. Figure 1 shows a scanning electron microscopy (SEM) micrograph of a silica obtained in this way. The structure seen in the picture reflects the droplet order in the original emulsion, which is rather well developed but not perfect because the droplets were somewhat polydisperse.

Most metal alkoxides react much more vigorously with water than silicon alkoxides. Aqueous emulsions are therefore incompatible with those alkoxides since they lead to

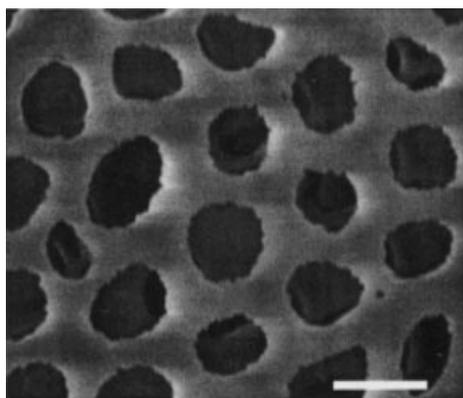


Fig. 1. Scanning electron micrograph of uniform macroporous silica. A piece of the sample, which had the form of a pellet, was broken off and covered with a layer of Au/Pd to observe the structure inside. The pore volume is 85 %. The scale bar equals 1  $\mu\text{m}$ .

immediate precipitation of metal oxide particles without forming a cast of the droplets. In order to be able to template emulsions with other inorganic materials it is necessary to use non-aqueous emulsions.<sup>[12]</sup> We found that oil droplets can be stabilized in the highly polar liquid formamide by the triblock copolymer surfactant (ethylene glycol)<sub>20</sub>-(propylene glycol)<sub>70</sub>-(ethylene glycol)<sub>20</sub>.<sup>[10]</sup> The use of non-aqueous emulsions opens up the possibility of templating emulsions with a large number of inorganic materials. We prepared stable sols of titanium and zirconium alkoxides in formamide by modification with acetylacetonate and partial hydrolysis with water. Going through the templating process thus leads to porous titanium dioxide and zirconium dioxide, respectively. Figure 2 shows scanning

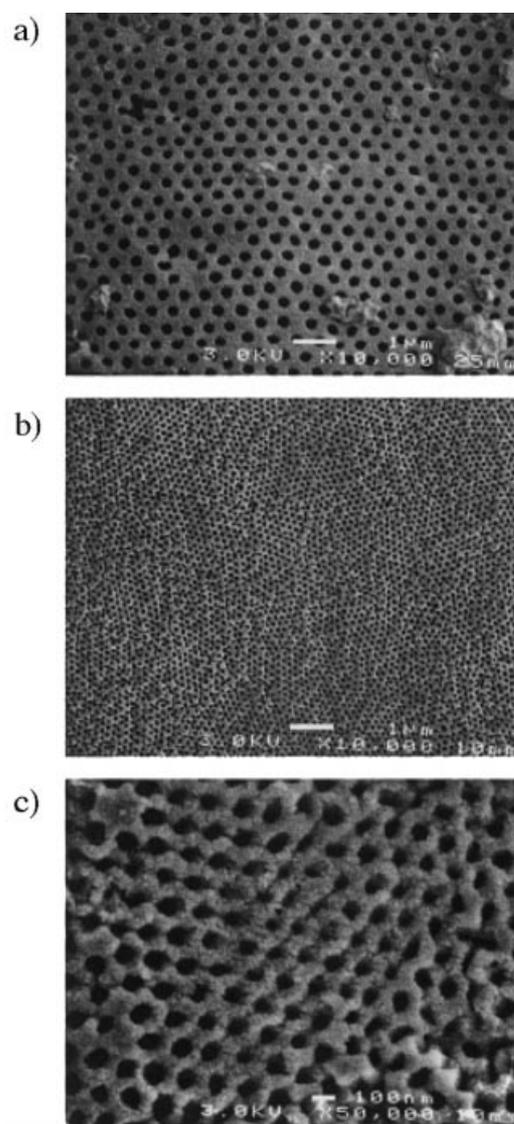


Fig. 2. Several SEMs of porous titania samples that have been fired at 1000 °C. The pores are highly uniform in size, allowing them to order in a regular lattice. a) A sample with a pore-to-pore distance of about 0.44  $\mu\text{m}$ ; scale bar equals 1  $\mu\text{m}$ . b) A sample with a pore-to-pore distance of 0.15  $\mu\text{m}$ ; scale bar equals 1  $\mu\text{m}$ . c) Close-up of the sample in (b) showing that the material is composed of tiny crystallites of  $\text{TiO}_2$ ; scale bar equals 100 nm.

electron micrographs of titanium dioxide with highly ordered arrays of pores. The graininess seen in Figure 2c indicates that the material is a very fine polycrystal. Powder X-ray diffraction showed that these crystallites have the rutile structure.

As an example of a macroporous organic material we made a gel of poly(acrylamide). The monomers acrylamide and methylene bisacrylamide were dissolved in the aqueous phase of a concentrated monodisperse emulsion stabilized by SDS. Some ammonium persulfate and tetramethylethylenediamine were added and the polymerization was initiated by heating to 60 °C. An SEM image of the dried product is shown in Figure 3.

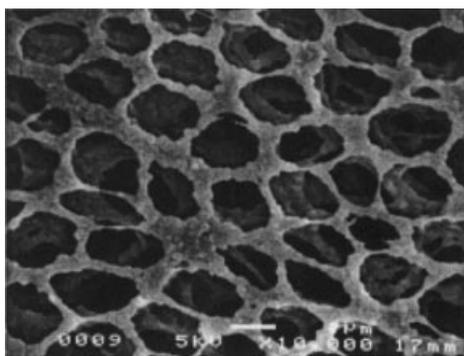


Fig. 3. SEM of a porous poly(acrylamide) gel. This sample is so porous that the holes are all connected through to each other. The scale bar equals 1  $\mu$ m.

All the organic and inorganic gels shrink by an amount of up to 50 % of their wet size during the drying stage of the preparation owing to removal of the solvent. Remarkably, the large shrinkage does not harm the pore structure of the resulting materials, as can be seen in the figures. The fact that the emulsion structure is successfully reproduced in the resulting materials makes emulsion templating a powerful technique for making structured porous materials.

## 6. Comparison with Other Templating Techniques

Our technique for producing *macroporous* materials bears a superficial resemblance to the molecular templating techniques from liquid-crystalline surfactant phases originally developed for making *mesoporous* materials.<sup>[13]</sup> In both techniques, an ordered surfactant-based system is used as a template for producing a uniform porous material. However, the two techniques are fundamentally different. When producing *mesoporous* materials, templating occurs on a molecular level with individual surfactant molecules directing the assembly of the silicate precursors. In contrast, no such molecularly directed templating occurs in the technique we describe. The only role of the surfactant is to stabilize the interface between the two immiscible liquid compo-

nents of the emulsion. As a result, our technique for making macroporous materials is typically less demanding than the templating techniques used for making mesoporous materials. We can fabricate macroporous materials made of inorganic materials such as silica, titania, and zirconia. We can also use our technique to produce organic macroporous materials made from organic polymers. In fact, a wide variety of materials, including optically and chemically active materials, could be incorporated into macroporous materials using the techniques we describe.

The molecular templating techniques introduced by Kresge et al.<sup>[13]</sup> have been extended so that increasingly larger pore sizes can be fabricated, with the largest reported sizes being in the range of 30–50 nm. These sizes are determined by the intrinsic dimensions of the liquid-crystalline phases that can be produced. Making liquid-crystalline phases with characteristic dimensions for templating larger than 50 nm is very delicate and difficult to achieve. The emulsion templating techniques we have described above represent a welcome addition to the techniques available for making porous materials, since they produce materials with pore sizes from 50 nm to 10  $\mu$ m, and thus greatly extend the range of pore sizes that can be fabricated controllably.

## 7. Conclusion

Emulsion templating allows one to make materials with uniform spherical pores in the size range 50 nm to 10  $\mu$ m. The range of pore sizes that can be made using this technique is determined by the range of sizes over which uniform emulsions can currently be made, i.e., currently from about 100 nm to 20  $\mu$ m. Advantages are that it is inexpensive and applicable to a wide variety of materials, which we demonstrated by making porous silica, titania, zirconia, and poly(acrylamide). Further improvements in emulsion processing,<sup>[14]</sup> and implementation of known techniques to manipulate particles in colloidal suspensions should enable the production of highly ordered, almost defect-free arrays of pores in many materials. We expect that this will lead to many new and useful materials.

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