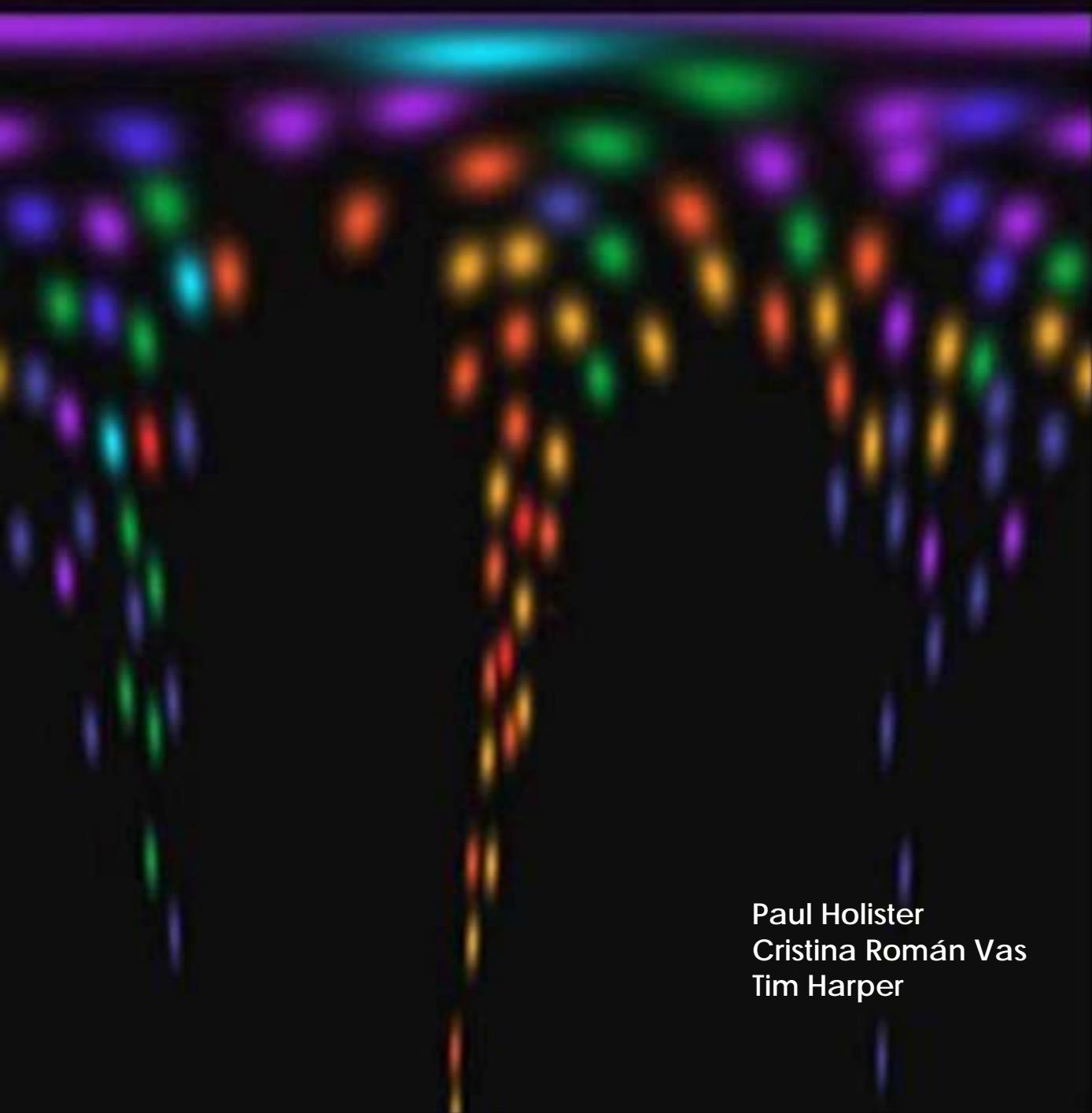




# Nanoporous Materials

Technology White Papers  
nr. 5



An abstract background image showing a dense, colorful array of small, glowing dots in various colors like purple, green, blue, and yellow, set against a dark background.

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October 2003

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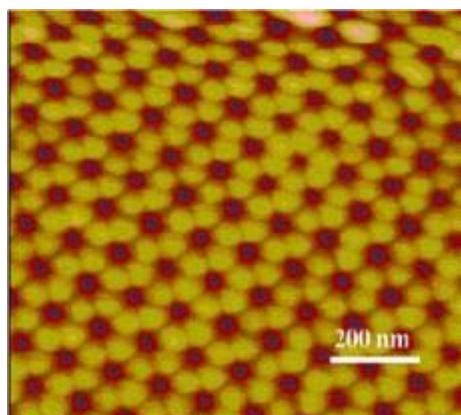
## Table of contents

Origin of content .....	6
Summary .....	6
Introduction to nanoporous materials .....	6
Nanoporous membranes.....	7
Bulk nanoporous materials .....	9
Glossary .....	11

## Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

## Summary



*Figure 1. Nanoporous membrane. Courtesy of MINT Center and Departments of Chemistry and Metallurgical and Materials Engineering, The University of Alabama.*

Nanoporous materials abound in nature, both in biological systems and in natural minerals. Some nanoporous materials have been used industrially for a long time. Recent improvements in our ability to see and manipulate on the nanoscale are transforming our use of these materials from the merely opportunistic to directed design. This is most strikingly the case in the creation of a wide variety of membranes where control over pore size is increasing dramatically, often to atomic levels of perfection, as is the ability to modify physical and chemical characteristics of the materials that make up the pores. The theoretical space of possible permutations for such materials is vast and will present many opportunities for the control of substances at the molecular and atomic levels for years to come.

Most importantly, this control will often be exercisable on macroscale quantities of material and can thus be expected to penetrate the chemical and pharmaceutical industries on an industrial scale.

Bulk nanoporous materials, which can better be visualized as diminutive sponge-like substances, are somewhat less exciting in terms of the range of possibilities and exquisite level of control, but nevertheless offer new applications on an industrial scale. Some of the materials, such as nanoporous silicon, are surprising in their range of properties and potential applications.

## Introduction to nanoporous materials

Nanoporous materials are all about holes that are less than 100 nm, although there are some interesting microporous materials with holes a little above this size and this report will not be too strict about the arbitrary 100 nm limit. Like many nanostructured materials, nanoporous materials abound in the natural world. The

walls of our cells are nanoporous membranes, although with a lot of added complexity. The petroleum industry has been using naturally nanoporous materials called zeolites as catalysts for decades, though the majority used now are synthetic. Recent years have seen significant improvements in understanding and making a variety of nanoporous materials.

It is convenient to divide nanoporous materials into bulk materials and membranes.

### Nanoporous membranes

Some of the most interesting applications for nanoporous membranes come from the ability of nanopores of certain sizes to let some substances pass and others not, or to force molecules like DNA to pass through one at a time, as examples given later will show. Controlling the size of these pores accurately is one of the technological challenges faced in making these materials.

There are a great number of ways of making nanoporous materials, so full coverage will not be attempted here but rather a selection to give some idea of the variety. Substances can be selectively leached out of a solid, leaving pores in their place, or combinations of polymers can be made to form into nanoporous solids by heating so that one polymer degrades and escapes. Combinations of polymers and inorganic materials, such as silica, are also being heavily researched. The sol-gel method can be used for making gel-based materials such as aerogels, where a gas is dispersed in a gel, producing a very light solid, sometimes only four times as dense as air. (The sol-gel approach works at room temperature whereas earlier methods of making aerogels used high temperatures.)

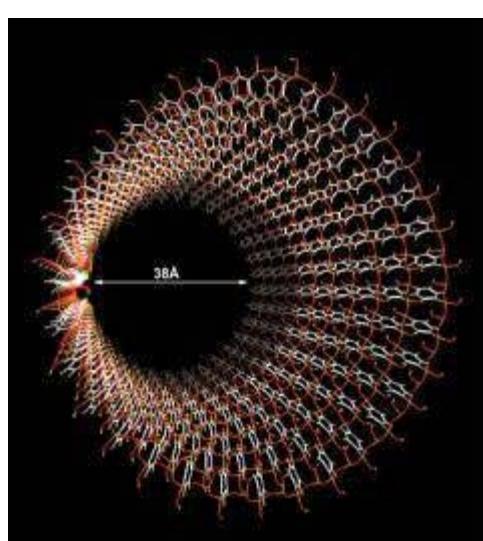


Figure 2. Ordered mesoporous organosilica hybrid material with a crystal-like wall structure. Courtesy of Frontier Research Group VII, Toyota Central R&D Labs. Inc., Japan.

An example of a promising recent development (early 2002) in organic/inorganic hybrid approaches comes from researchers in Japan who created a self-assembled structure out of silica and benzene with pores between 3 and 5 nanometers across. The most notable property of these materials is that the insides of the pores are perfectly ordered structures. The benzene can be functionalized (modified by the addition of chemical groups) without this regularity being lost, opening the possibility of creating a large variety of pores with internal structures that are precisely engineered at molecular scales.

Traditional lithographic approaches and soft lithography combined with etching can also create nanopores. An ion beam approach has been found capable of making pores in silicon nitride smaller as well as bigger.

From around mid-2001 a group of researchers in Florida, later working with others in Finland, started to quite regularly publish achievements based on a technique whereby a material is deposited on the inside of pores a few tens of nanometers wide in an alumina template. The process can be used to achieve specific chemical effects, to reduce the hole size, and even to create nanotubes of various materials by dissolving the original matrix.

This approach, which is also being explored by a number of other groups, is quite simple but extremely versatile, with the ability to control hole size quite accurately and use a wide variety of materials to achieve functionality controlling what materials pass through the holes, or what chemical and physical events occur inside the holes. Such membranes can selectively allow certain molecules to pass based on size, affinity for water, ionization and other properties. Materials captured inside the pores may also behave differently from their free state. The fluorescent properties of certain molecules, for example, have been enhanced by being fixed in 50 nm pores in an alumina matrix.

Other matrix materials have been used, such as polycarbonate membranes containing 10 nm pores that are then lined with gold and organic molecules called thiols, which have an affinity for gold. Controlling the acidity on either side of such a membrane allowed control over which materials could pass that extended even to similarly-sized proteins, by leveraging electrostatic properties.

Another approach to controlling pore sizes in membranes was developed late in 2000 in a joint project involving Sandia National Laboratories and the University of New Mexico. This uses ultraviolet light to break down molecules in a layer of self-assembled thin film silica that has a periodic structure. The product resulting from exposure to light causes the silica to solidify, following the same periodic pattern. Changing exposure alters pore sizes very consistently and the researchers believe it may eventually be possible to have sufficient control to create pores that are fine-tuned enough to separate oxygen from nitrogen molecules, which only differ in size by two hundredths of a nanometer.

One particular application of nanopores that has great potential is the approach suggested by a group at Harvard University of pulling single DNA or RNA strands through a nanopore using a voltage applied across the pore, and noting the change in current flow across the pore as a result of changes in ion flow, or changes in tunneling currents across the pore. These changes in current can potentially provide an electronic signature to identify each letter of the genetic alphabet as it passes through, thus sequencing the segment. The researchers claim the potential to sequence a complete human genome in a few hours. Initial work used lipid bilayers (similar to cell membranes) but these are not sufficiently stable for commercial use, and inorganic materials, with pores made using ion beam sculpting approaches, are being worked on. Development of a synthetic, controllable, nanopore is being pursued at the NASA Ames Center for Nanotechnology with the same objective in mind. These nanopore technologies should be fairly readily adaptable to protein analysis, although

the number of elements that need to be distinguished between (24 amino acids instead of four DNA bases) makes the task a little harder.

### Bulk nanoporous materials

The surface area of a solid increases when it becomes nanoporous, improving catalytic, absorbent, and adsorbent properties (adsorbing is like absorbing but the adsorbed material is held on the surface rather than inside). Zeolites, a range of naturally occurring or manufactured minerals with pores on the nanoscale and above, have been used as effective catalysts for decades. Surface areas of nanoporous solids are generally in the hundreds of square meters per gram.

In addition to catalytic effects, when materials are held inside nanopores their properties change in various ways, often unexpected, such as the freezing point of water rising markedly. Adsorbent and absorbent properties offer potential in environmental remediation, for example by mopping up heavy metals such as arsenic or mercury. These three properties are the most obvious offerings of bulk nanoporous materials but there are other less obvious properties that are potentially valuable.

Nanoporous solids have been made out of a wide variety of substances, including carbon, silicon, silicates, various polymers, ceramics, various metallic minerals and compounds of organic materials and metals or organic materials and silicon such as methylsilsesquioxane (one of the polyhedral oligomeric silsesquioxanes, or POSS, family used in nanocomposites and other applications).

Aerogels, highly porous materials that can be as little as four times as dense as air, contain pores of a variety of sizes but the distribution for silica aerogels tends to peak quite strongly around 5 nm radius, so these are truly nanoporous materials. Though fascinating, the low strength and brittleness of aerogels has limited applications, though traditional aerogels are robust enough to be used in applications such as catalysis and filtering, and also present interesting optical properties. The thermal insulating properties of aerogels could be exploited in double glazing, where strength is provided by the containing glass. However, more interesting applications would present themselves if strength could be improved and some research has shown ways of achieving this. Most notably, late in 2002 aerogels were created that were 100 times more resistant to breakage than conventional aerogels.

Nanoporous silicon, which is created by etching silicon with acid, has been found to be capable of stimulated light emission, as in lasers, and also holds promise as a biocompatible material. One issue with such silicon for optical applications is its instability, but a group at Purdue University has managed to give it a stabilizing coating using a reaction initiated by light. The instability is advantageous in other applications, though, such as biodegradable medical implants, whether structural or for drug delivery.

Nanoporous silicon in fact has a number of interesting properties, such as having a refractive index that can be changed by light and the ability to emit acoustic waves

through thermal stimulation. It was also found, in late 2002, to be capable of effective field emission (producing a stream of electrons) without the presence of a vacuum.

Activated carbon is an example of a nanoporous material that, like zeolites, has been in use for a long time. It is produced by a very large number of companies, which will not be covered in this report except where particular novelty in manufacturing or application is seen. Researchers in Korea, for example, have developed a templating technique using silica nanoparticles that can create activated carbon with uniform 8 nm and 12 nm pore sizes. The resulting material showed adsorption greater than 10 times that of commercial activated carbon. Removing metal ions from a crystalline matrix containing both metal and carbon allows the creation of a variety of novel nanoporous carbon materials depending on process conditions. This approach is being commercialized by the Swiss company Skeleton Technologies.

Nanoporous carbon with new geometries has been created by other methods. A multinational group of researchers created, in early 2002, a form of highly nanoporous carbon with a fractal internal geometry (fractals are patterns that show similar structures at different scales, such as coastlines or the branches of trees). The group believes the material has potential for methane (natural gas) storage for vehicles.

A group of Italian and British researchers created, in late 2002, a form of carbon that belongs to a group of materials that had been hypothesized a decade earlier, and dubbed schwartzites. The material uses carbon rings containing more than 6 carbon atoms (which create the flat hexagons in graphite) to create an internal structure with negative curvature that is highly porous, with pore sizes in the 50-600 nm range, much larger than in activated carbon.

A completely new class of nanoporous materials has recently been developed, being a set of flexible materials that are part polymer and part ceramic (developed at Cornell). When heated the material becomes nanoporous, with pore sizes between 10 and 20 nm and excellent uniformity, which results from the use of self-assembly to create a material that is virtually atomically perfect.

Zeolites, although long used, are still a subject of research. In late 2002 a modified zeolite was shown to be the first example of an interesting class of materials called electrides that are inorganic and stable at room temperature. Electrides have a positively-charged structure with charge being balanced in the form of an electron 'gas' in the pores. Apart from the obvious catalytic applications, the materials

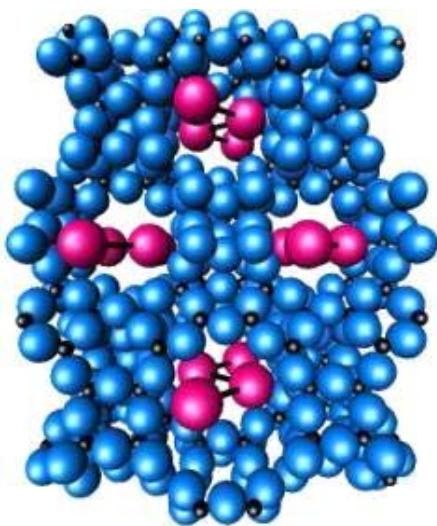


Figure 3. Cesium atoms forming zigzag chains of positively charged ions within a zeolite. Image courtesy of Prof. Valeri Petkov, Central Michigan University, USA.

have interesting electrical, magnetic, and optical properties.

## ***Glossary***

### ***Mesoporous***

Terminology for nanoporous materials can be confusing because there is an alternative system in widespread use that bears no particular relation to metric prefixes. The system is that of the International Union of Pure and Applied Chemistry (IUPAC), where pores of less than 2 nm in diameter are termed micropores, those with diameters between 2 and 50 nm are termed mesopores, and those greater than 50 nm in diameter are termed macropores.

### ***Photonic crystal***

Photonic crystals are structures containing elements that repeat a pattern at the scale of electromagnetic wavelengths (such as those of visible light, for example) that causes a regular variation in optical properties. In the overall material, this regular variation leads to a band gap, i.e. a certain frequency range of light cannot pass through the crystal. This phenomenon enables the creation of structures that exert remarkable control over light, doing things that are impossible with conventional optics, such as making waveguides with sharp 90 degree bends in which no light is lost, or 'boxes' in which light can be trapped. Photonic crystals are often described as the optical equivalent of semiconductors; the word photonic is itself analogous to the word electronic.