

THE ARCHITECTURE OF THE VERY SMALL

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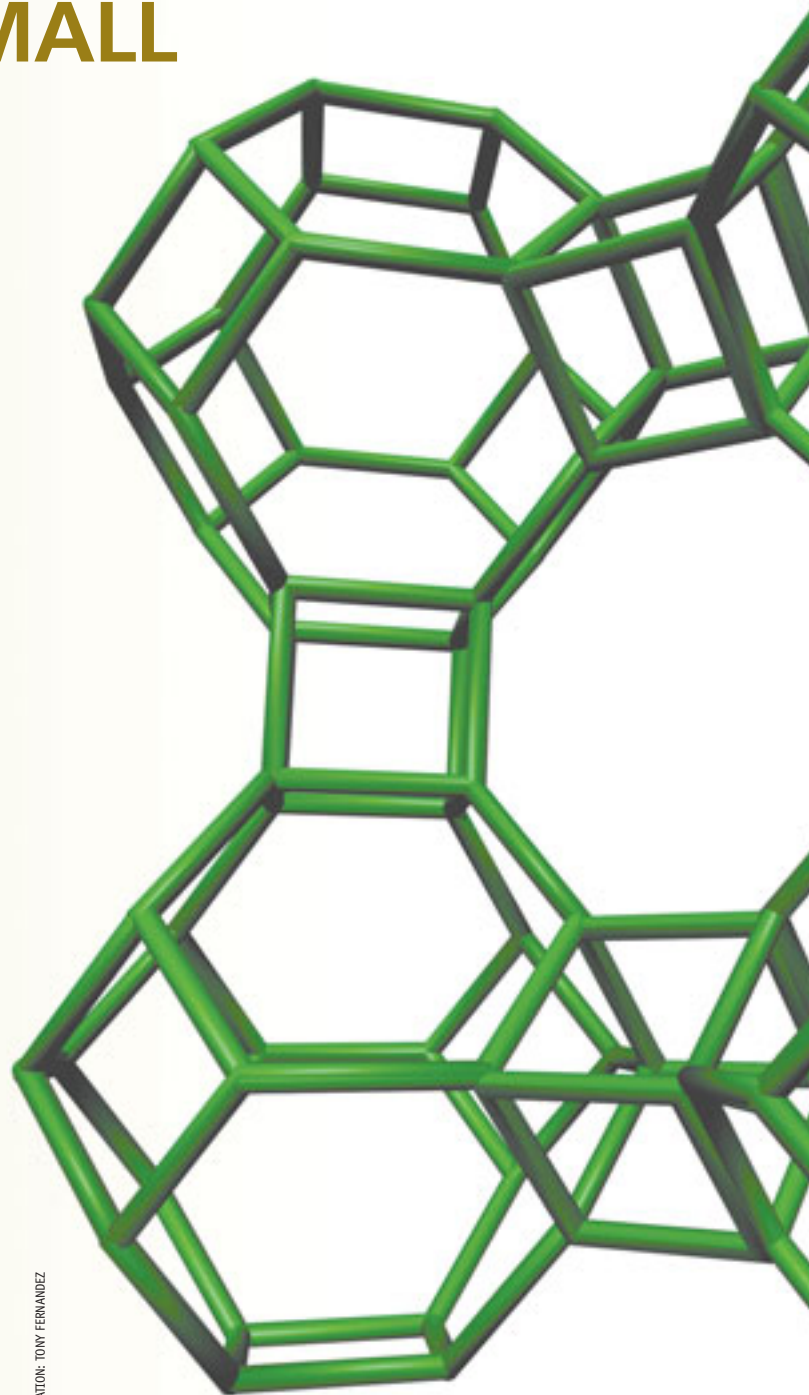
For nanostructured solids, it's not just the chemistry, it's the way they're put together.

Chemists think in terms of formulas. By decoding the right combination of letters, numbers, symbols, and parentheses, they can get a fairly good idea of a molecule's structure. In the solid-state world, however, chemical formulas are only a beginning, and when the structures get complex, formulas tell you very little. For many of the most interesting new nanostructured solids, it's the architecture that counts.

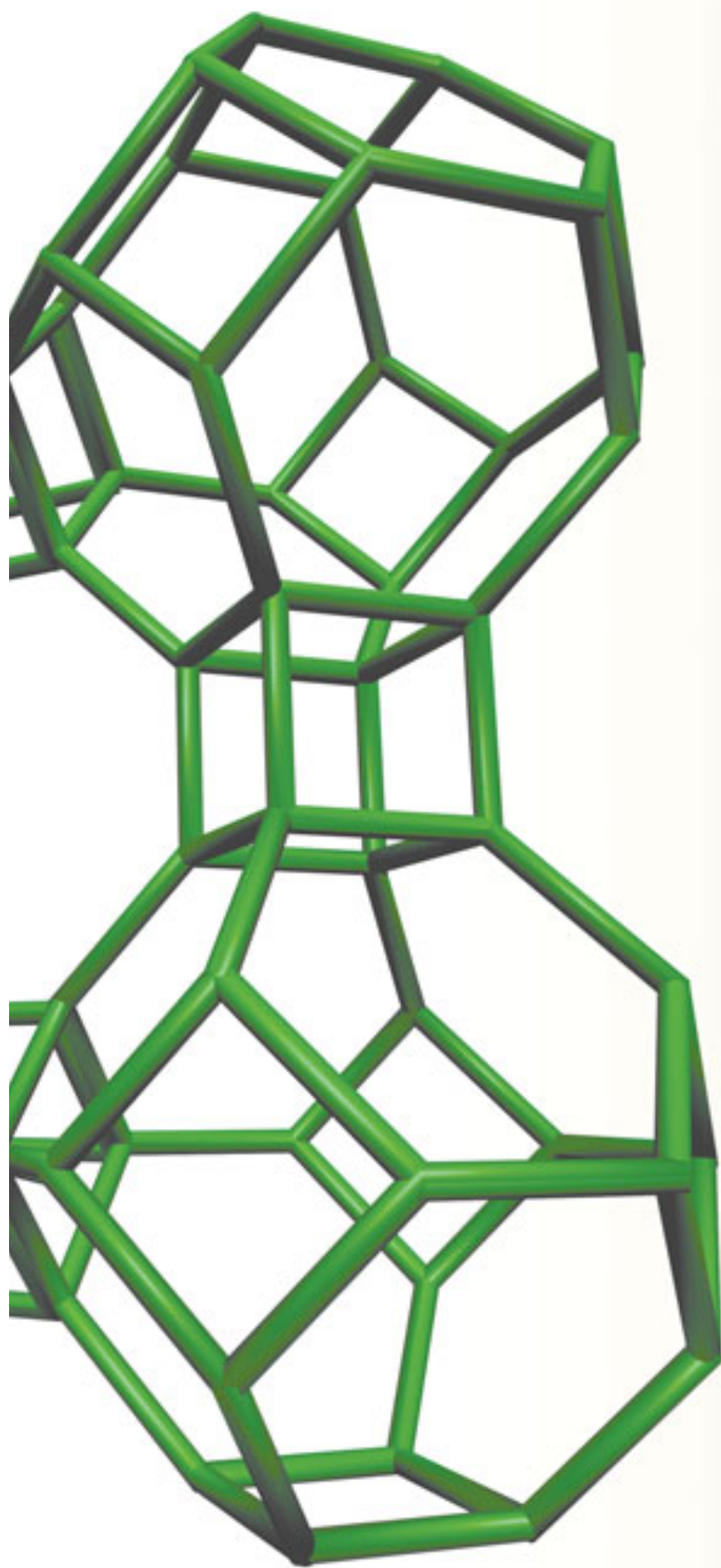
Take a familiar example: silica. The formula SiO_2 is an equally accurate description of beach sand, laboratory glass, some petroleum cracking catalysts, and several host materials for drug or nutrient delivery. Add a little water, and you have opals, or perhaps an amorphous gel. The difference between parking lot gravel and the latest nanostructured wonder is all in how the building blocks are put together.

(Feed)stock Exchange

After quartz and glass, the silicate phases chemists are probably most familiar with are the molecular sieves. Organic chemists use molecular sieves as drying agents, and petrochemical specialists rely on "sieve" to separate hydrocarbons of various weights and to act as solid acids in oxidation reactions. Molecular sieves, synthetic variations on the naturally occurring minerals known as zeolites, are made by mixing finely divided silica or metal silicates with water and organic "templates", typically small-molecule amines. Heating this mixture in an autoclave produces an amorphous gel, which is dried to produce crystalline silicate



SILICON DIOXIDE ILLUSTRATION: TONY FERNANDEZ



frameworks containing ordered networks of channels and cages a few tenths of nanometers across. Initially, these void spaces are filled with water and organic molecules left over from the synthesis. If the host framework contains a mixture of differently charged cations (typically Si^{4+} and Al^{3+}), the void spaces contain alkali metal, alkaline earth, or hydrogen ions to provide charge balance.

Removing the synthesis molecules and ions from the molecular sieve channels by heating or ion exchange “activates” the molecular sieve for a wide variety of applications. Neutral frameworks, typically aluminum phosphates or pure silica phases, are used to separate small molecules, which can pass through the channels and cages, from larger molecules; hence the name “molecular sieves”. Neutral frameworks can also be used as encapsulating agents for drug delivery or nutritional supplements. Substituting aluminum, manganese, or other cations for some of the silicon atoms in the framework produces charge imbalances that convert the framework into a Lewis acid. The counterions contained in the channels and cages of these phases can be used as ion exchange media in water softeners or as mineral nutrients for plants. Alternatively, organic feedstocks can be flushed through the channels, where they briefly adhere to the acid sites and undergo oxidation or functionalization reactions before exiting the sieve. Molecular sieve-type solid acids are a high-volume commodity in the petrochemicals industry. These materials can be regenerated repeatedly by heating or ion exchange, making them an environmentally friendly alternative to solution-phase processing.

Mesoporous silicates, which first appeared in the 1990s, are a logical extension of the microporous molecular sieve phases. The silicate frameworks in mesoporous solids surround ordered arrays of cylindrical pores several nanometers across. Cylindrical micelles made from long-chain surfactant molecules serve as

bottle-brush-shaped templates. The silicate frameworks themselves are typically disordered, in contrast with the crystalline frameworks characteristic of the microporous solids. Mesoporous silicates have been used for similar applications as the microporous solids—encapsulating materials, catalyst supports, and molecular sieves—but the larger pore volumes open up new and more complex applications involving larger guest molecules and more complex interactions.

Disorderly Conduct

Moving from microporous solids, with their crystalline frameworks enclosing ordered arrays of channels, to mesoporous solids, with disordered frameworks enclosing ordered arrays of channels, the next step is mesostructured cellular foams (or sponges), where nothing is orderly. This randomness is actually an advantage for some applications, such as bifunctional catalysts, where accessible surface area is the main consideration. The pore spaces in a typical foam can be several tens of nanometers across, allowing small molecules to pass through with diffusion rates approaching those in an open medium (1). In addition, the pore spaces form a three-dimensional connected network, so that if one channel becomes blocked, the flow of molecules merely shifts to another channel.

Aerogels, extremely porous foams that can contain more pore volume than solid material, permit the high flow-through rates required for sensor applications, charge storage materials, and electrocatalysis. Multifunctional catalyst foams contain two or more functional entities that provide different contributions to the reaction that produces the end product. For example, metal nanoparticles dispersed on an active oxide phase provide chemisorptive activation (from the metal) and oxygen-atom transfer (from the oxide) (1).

Further complexity is added when the aerogels are functionalized with guest molecules. Ligand-stabilized colloids, such as thiolated metal clusters, can be used to introduce uniformly sized guests into the host framework. Gold-titania composite aerogels have been used to convert 250–400 $\mu\text{mol/s}$ of CO to CO_2 per gram of gold at room temperature (1). In a typical supported-metal catalyst, small metal particles are dispersed over large areas of the oxide substrate, but recent catalysts have used a more equal distribution of metal and oxide particles. This maximizes the amount of contact between the metal and the oxide surface, and reduces the distance that the reactive species must travel between phases. According to Debra Rolison of the U.S. Naval Research Laboratory (www.nrl.navy.mil), the catalyst is “no longer a metal ‘flea’ riding an oxide ‘boulder’, but a multiparticulate arrangement of equals.” Similarly, carbon black (which has a very high surface area) modified with a platinum colloid is a much more active oxidizer of methanol when the colloid is nanoglued in place with silica sol to form a composite aerogel.

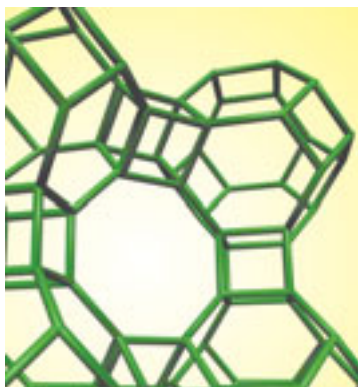
Carbon aerogels, which are electrically conductive, present interesting possibilities for ultralight capacitors. Some developmental work has been done on using stacks of carbon aerogel electrodes to remove pollutants from water (2). Applying an electric field causes ionic pollutants, including heavy metals and radioisotopes, to cling to the surface of the electrode, and the

cell effluent is deionized water. Researchers at Lawrence Livermore National Laboratory (www.llnl.gov) tested this method on local groundwater and showed that chromium levels could be reduced to 2 ppb, well below the regulatory limit of 11 ppb.

Totally Tubular

Structural design on a nanometer scale is the current challenge facing materials architects. Researchers are working toward creating solid architectures to fine-tune the light-propagating properties of photonic materials in much the same way that semiconducting materials use chemically tuned electronic band gaps to control the flow of electrons. Photonic crystals have repeat distances on a length scale similar to the wavelengths of light in the visible-to-IR range, and their chemistry and structure dictate the distribution of the energy levels that the photons may occupy.

“Inverse opals”, solid frameworks surrounding an array of void spaces or spherical templates, have proved to be one of the more easily synthesized structures for visible-light photonics. Inverse opals are a “photonegative” version of the opals found in nature, which consist of densely packed spheres of noncrystalline hydrated silica. In gem-quality opals, the spheres are fairly uniform in size. The silica chains that make up the spheres are disordered, but the spheres themselves are packed in an orderly fashion, like oranges stacked in



a crate. The sizes of the spheres are on the same order as the wavelength range for visible light, and the ordered packing creates a diffraction-grating effect. The result is the bright flashes of color characteristic of “fire opals”. Inverse opals can be used to manipulate light as well, with the periodic array of void spaces and the solid framework acting as the grating.

Recently, researchers from the Max Planck Institute for Coal Research (www.mpi-muelheim.mpg.de/kofo/english/mpikofo_home_e.html) succeeded in building an inverse opal from dielectric TiO_2 cylinders to create a material with a calculated band gap that has a lower frequency than existing reverse opals, and the possibility of creating two complete band gaps in the same material (3). This type of structure opens up possibilities for controlling the photonic band structure of optical materials in a predictable way.

The titania-filled opals were prepared by first creating a synthetic “opal” out of 270-nm polystyrene spheres. A solution of titanium isopropoxide in ethanol was poured into the spaces between the spheres, and after the mixture was air-dried, it was heated at 300–580 °C for several days to burn off the polystyrene. The result was a network of cylindrical structures surrounding air-filled void spaces (Figure 1). The cylinders were thicker than predicted on a strictly geometrical basis for void-filling between spheres, and the researchers found that they could increase the radii of the cylinders by increasing the concentration of the precursor solution and burning off the polystyrene at a lower temperature. X-ray diffraction patterns of the resulting cylinders indicated that they were made from very small particles of TiO_2 in the anatase form, which is not the most common form in nature. Further, they found evidence that the cylinders are likely to be porous, and they are investigating this possibility.

Since the purpose of making the reverse opals was to investigate their optical properties, the researchers calculated the distri-

bution of the photonic energy bands to chart the distribution of photon frequencies throughout the solid. They found one gap in the energy bands where they expected it, based on similar reverse opal materials, but they also found another band gap that had not been observed before. This second band gap could occur alone or in addition to the expected band gap, depending on the parameters used for the calculation. For the complete double band gap to occur, the material needs to have a critical refractive index greater than 3. Thus, the titania skeleton structure has only "pseudogaps", because its refractive index is 2.5 or lower, depending on the porosity of the cylinders. Other materials, such as silicon or germania, could be used to construct similar cylinder frameworks having high enough refractive indexes in the IR wavelength range to exhibit the double band gap. Materials such as gallium phosphide and cadmium telluride could be used to make frameworks having the double band gap in the visible light region. Research in this area is in the early stages, but the discovery of multiple band gaps opens up several interesting possibilities for fine-tuning optical materials.

Fixing up the Guest Room

Recently, researchers at Clark University (www.clarku.edu) produced a crystalline solid where the host and guest molecules interact to form a molecular switch (4). The host framework is a flexible network formed by rhombohedral grids of iron atoms linked by *trans*-4,4'-azopyridine (azpy) units. Each iron atom is surrounded on four sides by azpy groups, and two thiocyanate (NCS) groups complete the octahedral coordination. The starting compound is made in ethanol solution, and the resulting crystals contain ethanol molecules in alternating pores, in what the authors describe as a "chessboard" configuration. Heating the crystals to 100 °C causes the ethanol to leave the host framework, which then "scissors" into a more compact configuration. Reintroducing the ethanol causes the structure to revert back to its expanded state. The ethanol can be removed and reintroduced repeatedly without shattering the crystals.

The magnitude and reversibility of this structural change would be remarkable enough, but magnetic susceptibility and Mössbauer spectroscopy studies indicate that the ethanol guest molecules play a key role in the electronic and magnetic properties of the host framework as well. In the fully loaded state, half of the iron atoms are hydrogen-bonded to the ethanol molecules via their NCS groups. Between 300 and 150 K (23 to -123 °C), all of the iron atoms in the structure are in a "high spin" state; that is, the spins of only two of the six valence electrons are paired. Two of the remaining four electrons remain at the same energy

level as the spin-paired electrons, but the two electrons that would have been paired with them occupy a higher energy level. In addition to being paramagnetic, the $\text{Fe}_2(\text{azpy})_4(\text{NCS})_4 \cdot \text{EtOH}$ crystals are dark red, typical of high-spin iron compounds.

As the temperature is lowered, the magnetic moment decreases, reaching a constant value below 50 K (-223 °C). At this low temperature, half of the iron atoms have undergone "spin crossover", moving to a "low spin" state with all six of the valence electrons occupying the same energy level, arranged in three spin-up/spin-down pairs. True low-spin iron compounds are diamagnetic and tend to be pale yellow to colorless, but the Clark group found that only half of the iron atoms associated with the ethanol molecules underwent spin crossover at low temperatures. When the ethanol was removed from the structure, all of the iron atoms remained in the high-spin state, even at low temperatures, indicating that the reason for the spin crossover effect was either the hydrogen bonding effect or the framework distortion caused by the presence of the guest.

Substituting methanol or propanol for the ethanol guest molecules produced similar magnetic effects, although the change in

magnetic moment with temperature varied somewhat with the type of guest molecule introduced. This type of molecular switching behavior could eventually be applied to making molecular sensors that change colors, magnetic properties, or even size and shape, in the presence of a particular compound.

Silica is SiO_2 , whether it's in massive quartz crystals or aerogels that are mostly air. In inverse opals, the void spaces are just as important as the solid framework. And flexible organo-iron frameworks let guest molecules come and go without falling apart. Which only goes to show that chemical formulas describe the bricks and mortar for the nanoengineered "buildings", but the solid structures are the architectural blueprint.

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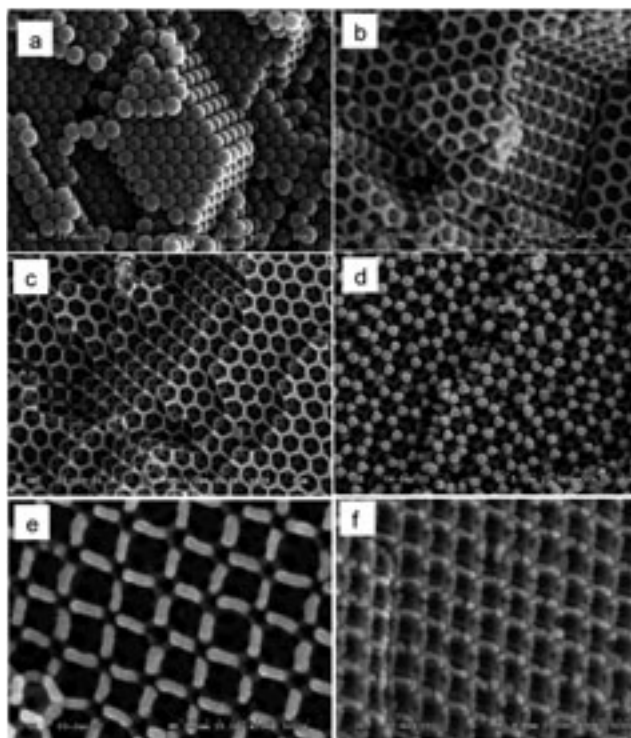


FIGURE 1: SEM pictures of the PS opal (a) and of skeleton structures (b-f). The pictures (b-f) depend on viewing direction and sample preparation conditions. (Adapted with permission from Ref. 3.)