



## PERSPECTIVES: MATERIALS SCIENCE

# Opals in a New Light

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From graphite, to fullerene ( $C_{60}$ ), and on to carbon nanotubes, the number of intriguing material properties grows with the number of carbon atoms in the building blocks. This sequence has now been extended with “cubic graphite,” a structure with a unit cell of several hundred nanometers. On page 897 of this issue (1), Zakhidov *et al.* describe the synthesis of a conductive, graphite “inverse opal” together with similar structures consisting of amorphous carbon and diamond made with artificial opals as the template. These regular carbon structures hold great promise as both macroporous materials and photonic crystals.

Natural opals consist of a regular three-dimensional (3D) crystalline array of colloidal silica spheres several hundred nanometers in size. Nowadays, artificial opals or colloidal crystals are made from sufficiently concentrated monodisperse particles (that is, they do not differ too much in size). Usually, the colloidal crystals are grown from readily available dispersions of silica or latex spheres. Recently, several groups have realized that the interstices in a colloidal crystal can be filled with all kinds of organic and inorganic precursors and that regular macroporous materials can be made if the templating spheres could be removed without destroying the crystalline order. Several approaches have proved successful in this respect: evaporation of emulsion droplets from a not completely crystalline sphere packing (2) and, from fully crystalline lattices, combustion of latex spheres (3–5) and dissolution of silica spheres (1). In all cases, the filler material stays behind in polycrystalline form (titania, zirconia, or diamond) or amorphous form (silica, alumina, or carbon) either as a regular 3D “air-sphere” structure or as a not completely filled “shell” structure (see

figure). The cubic graphite structure made by Zakhidov *et al.* is special because the graphite sheets of ordered carbon atoms are themselves ordered with the symmetry of the dissolved face-centered cubic colloidal crystal array (1).

These regular macroporous materials form a natural extension of the recently developed molecular templating techniques from liquid-crystalline surfactant phases to make mesoporous materials. As such, they are important for processes such as catalysis, sorption, and separation. It is just a matter of time until the method to make mesoporous structures is com-

terfly wings and peacock feathers, this iridescence is due to the interference of light that is scattered by a photonic crystal or a regular dielectric structure with feature sizes of the light's wavelength.

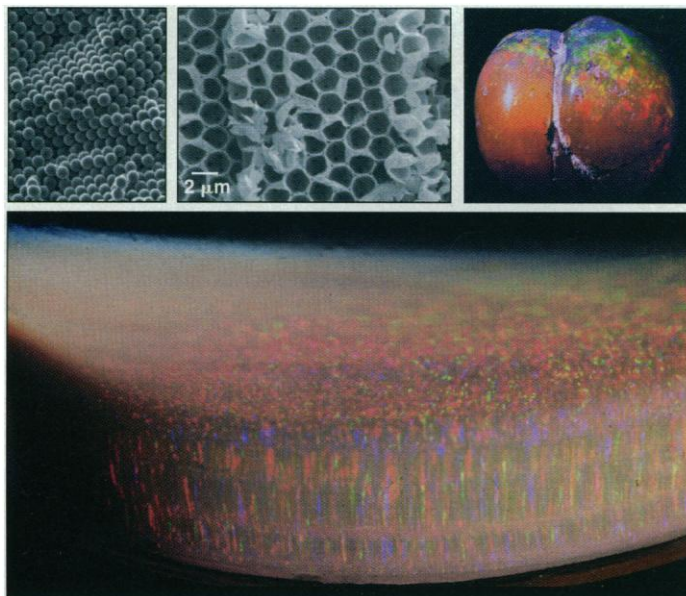
Photonic crystals promise to become as important to the progress of optical devices as semiconductors were to the development of electronic devices. In 1987, Yablonovitch and John both independently proposed investigating the design of 3D structures in which the propagation of photons with a certain energy would not be allowed, just as there is a band of forbidden energy (the band gap) for electrons in a semiconductor (7). Subsequently, it has been shown both theoretically, and experimentally for microwave radiation, that such structures do exist (8). Furthermore, theory predicts that novel optical properties such as inhibition of spontaneous emission and lossless waveguides with

tight bends are possible (7). However, 3D structures with a complete band gap for the much more important near-infrared or visible light have not yet been made because with conventional microlithography techniques it is very hard to make structures with both feature sizes well below 1  $\mu\text{m}$  and a thickness that extends over a few layers (8).

Colloidal particles that can self-organize into colloidal crystals and can be chemically modified are, therefore, natural building blocks for photonic crystals. Unfortunately, it has been shown theoretically that a face-centered cubic colloidal crystal, which is relatively easy to make, does not possess a complete photonic band gap. Furthermore, the relative refractive index contrast needs to be larger than  $\sim 2$ , and colloidal spheres with such large con-

trasts, like  $\text{TiO}_2$  with contrast  $\sim 2.6$ , are hard to make monodisperse enough. The reverse air-sphere structure, however, has been predicted to have a complete band gap. This is why the recent synthesis of the beautiful inverse  $\text{TiO}_2$  air-sphere structures (4, 5) has been a breakthrough, creating dielectric structures with perhaps not a full band gap, but certainly very strong photonic manipulation strength.

The first photonic effects on the emission of a fluorescent dye placed inside a colloidal crystal have been observed for much lower contrast than for titania in air (9). The conducting photonic carbon crys-



**Opal and inverse of opal.** (Bottom) Colloidal crystal (or artificial opal) grown from a dispersion of silica spheres (crystal height is about 2 cm). (Top: left to right) Scanning electron micrograph of the same crystal (sphere diameter, 300 nm), titania “shell” structure made by opal-templating (5), and natural opal (several centimeters in size).

combined with the synthesis of the regular macroporous materials, leading to even more possibilities. The first steps along these lines have already been taken by Antonietti *et al.* (6).

The 3D regularity of these materials is potentially of even greater importance for photonic applications, because it allows for the manipulation of the propagation and spontaneous emission of photons in the visible range of the spectrum. Opals are valued as gemstones because of their bright iridescent colors, which change as a function of the viewing angle (see figure). Just like the beautiful colors on many but-

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tals might open up new possibilities, such as larger band gaps, that are not possible with pure dielectric materials as has been shown in experiments and theory for microwave radiation [see references cited in (8)]. However, absorption of the metallic structures, as is the case for photons in the visible, could limit these possibilities. The effects of absorption, which will become important for fluorescent materials placed inside photonic crystals as well, have hardly been studied theoretically and not at all experimentally. This situation will undoubtedly change soon.

It is clear that the colloidal templating route is substantially cheaper than conventional lithographic methods to produce 3D structures with submicrometer feature sizes and that now truly 3D structures with high contrast and even metallic properties are easily obtained. Moreover, with yet another templating approach,

this time extending epitaxial crystal growth procedures to the colloidal domain, my colleagues and I have been able to grow large colloidal single crystals and direct their structure and orientation (10). The time has now come to use these methods, or most likely combinations of them, to make materials that demonstrate some of the above-mentioned promise and potential. For instance, one can easily imagine using inorganic colloids, possibly fluorescently labeled, in the processes that use organic spheres as templates. And vice versa, one could use latex spheres in the process that dissolves silica. With such combinations, the air-sphere crystals could be doped by placing a few dielectric particles in the air spheres to create dielectric defects, for instance, to open up a narrow transmission path in the band gap. In the same way, the conductive crystals could be made into

perhaps even more versatile metallo-dielectric crystals. Guided by theoretical calculations, it will probably not take long for these opal-based photonic crystals to be seen in a new light.

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#### PERSPECTIVES: THIN-FILM PATTERN FORMATION

## The Artistic Side Of Intermolecular Forces

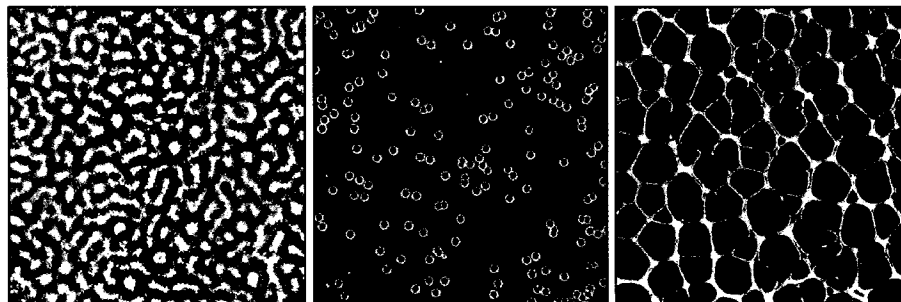
Günter Reiter

Liquid films thinner than about 1  $\mu\text{m}$  are often unstable and develop various morphologies (see figure). The stability of such films may be essential, for both numerous applications and various scientific experiments, and so this behavior can be rather annoying. As reported on page 916 of this issue, Herminghaus *et al.* (1) have recently addressed the question of why such films are unstable. They have presented some convincing results that indicate the relevance of intermolecular forces for what they called "spinodal dewetting." It is similar to the process of spinodal decomposition, in which a binary mixture becomes unstable and moves along a cusplike curve (spinode) toward phase separation.

There is a long-standing debate about the factors responsible for the instability of thin liquid films. On the theoretical side, Scheludko and Vrij proposed some 30 years ago (2, 3) the possibility of an intrinsic instability induced by long-range van der Waals forces across the film. However, most previous experimental observations of unstable films were simply attributed to rupture of the films induced

by defects such as dust particles, which, in turn, resulted in dewetting. Thus, attempts have been made to eliminate defects. Only recently have several model experiments (4–7), mostly with polymers, allowed the exclusion of initiation of dewetting by defects. Nonetheless, in many cases, it is still not clear what kind of interactions were responsible for the instability (3, 4). This is because several different morphologies, in particular wave patterns and isolated circular holes (see figure), evolved from such an instability. It was erroneously assumed that these different morphologies necessarily imply that dif-

ferent processes had generated them, mainly because early linear theories (3, 8) of spinodal dewetting were unable to predict the various possible patterns. Undulation patterns were taken as signs of spinodal dewetting, whereas the formation of isolated holes was thought to reflect an instability induced by defects or heterogeneities (5, 9). The major achievement of Herminghaus *et al.* (1) is that they have now shown that the same process—spinodal dewetting—can result in different patterns if the long-range van der Waals forces are coupled with various short-range interactions. Thereby, the nonlinearities of the "wetting forces" are modified. This allows the formation of holes in gold films for strong nonlinearities (that is, the long-range interactions are only weakly modified by a thin chromium layer) and undulation patterns if the strong attraction of the van der Waals forces, especially



**Shifting shapes.** Different morphologies exhibited by unstable thin polymer films. (Left) Polydimethylsiloxane film under water on a silicon substrate covered with a layer of end-grafted identical molecules. (Middle and right) An early and a late stage of dewetting of high molecular weight polystyrene on nonwettable silicon substrates. None of these states represents an equilibrium situation that would be isolated droplets. Images are 200  $\mu\text{m}$  by 200  $\mu\text{m}$ . Lighter colors represent thicker sections of the sample.

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