at Delft used a linking molecule for the controlled immobilization of the redox enzyme glucose oxidase (GOx), which catalyzes the oxidation of β-D-glucose to D-glucono-1,5-lactone, on the outer wall of a semiconducting carbon nanotube (CNT) to create a nanosensor that acts both as a reversible pH sensor and as a sensor capable of measuring GOx activity. CNTs, 600 nm in length on average, were grown using chemical vapor deposition on degeneratively doped silicon wafers that had a 200-nm thermally grown oxide layer. The researchers conclude from atomic force microscopy images that GOx molecules are immobilized specifically on the SWNTs with a density of about one GOx molecule every 12 nm. Electrodes, composed of a 30-nm gold layer and a 5-nm titanium adhesion layer, were deposited onto the SWNTs using electron-beam lithography. The liquid solution, in which all electrical measurements were made, acts as a very efficient gate for the immersed semiconducting SWNTs.

The researchers show that a substantial decrease in the conductance of SWNTs results from the attachment of only about 50 GOx molecules, thereby demonstrating the potential for sensing the presence of GOx proteins. The researchers said that the decrease in conductance cannot simply be due to electrostatic gating by GOx; they propose that it results instead from the decrease in the tube capacitance. They cite numerical estimates of the decrease in conductance, which agree with the experimental measurements, in support of the group's hypothesis.

The conductance of GOx-coated SWNTs is also strongly dependent on pH. The researchers believe that their nanotube sensors are sensitive to and can measure pH changes with an accuracy of 0.1 pH. They attribute this sensitivity to charged groups on the GOx molecules, which become more negative with increasing pH. This results in a decrease in the electrostatic gate voltage and an increase in the SWNT conductance. In addition, the researchers report that GOx-coated SWNTs also appear to be sensitive to glucose levels. However, quantitative reproducibility of the effect was hampered by substantial low-frequency noise.

The researchers said that higher-mobility devices prepared from short SWNTs (~20 nm) may provide a powerful tool for enzymatic studies with the ability to measure the activity of even a single redox enzyme. In addition, they look forward to new nanotube biosensors that detect in real time a variety of biomolecules without the need for labeling.

STEVEN TROHALAKI

Biological Template Controls Organization of Au Nanoparticles

Using microorganisms as biological templates is a promising way for assembling nanoparticles into ordered macroscopic structures with architectural control at the nano- , micro-, and macroscopic length scales, but control across multiple length scales is challenging. Different microorganisms such as viruses, bacteria, and fungi can be used as templates for nanoparticle deposition. In the May 23 issue of *Angewandte Chemie*, a group of researchers led by Chad A. Mirkin at Northwestern University demonstrates how fungi (*Aspergillus niger*) can be used as templates for assembling gold nanoparticles into high-surface-area semiconducting materials.

Gold nanoparticles of 13-nm diameter were obtained after the reduction of $HAuCl_4$ (1 mM) by trisodium citrate. Prior to assembly, the surfaces of the nanoparticles were modified with alkylthiol-capped oligonucleotide strands; then the modified Au nanoparticles were added to a culture solution consisting of filamentous fungus spores, making a red colloidal solution. During germination, the fungi grow through extension and branching of hyphae (i.e., fine, threadlike filaments). During fungal growth in the culture solution, the microorganisms accumulated gold nanoparticles on the surfaces of the hyphae, turning the red colloid colorless after ~64 h. Air-dried and compressed into thin films, the fungal mats exhibited a golden hue and faint metallic gloss resembling bulk gold. Scanning electron microscopy studies showed that the compacted material preserves the fibrous structure of the *Aspergillus niger* mycelium. Electrical-transport measurements on this material exhibited Arrhenius-like temperature dependence with an activation energy of 1.62 eV.

The structures of single fibers were studied by transmission electron microscopy, revealing that, in vacuum, the hyphae with nanoparticles on the surface collapsed to form thin, nanoparticle-coated, belt-shaped structures. In order to preserve the original structure of the hybrid material, the hyphae coated with nanoparticles were dried in acetone and embedded in an epoxy resin. An ultramicrotomed cross-sectional slice of a fungal fiber in epoxy showed a nanoparticle-coated ring structure 3–4 μm in diameter. The researchers reported that a second layer of nanoparticles can be hybridized with the first layer by using nanoparticles with oligonucleotides that are complementary to the first set of particles. This allows the introduction of a secondary structure into the material, they said.

Although the researchers indicate that they do not currently know the nature of the interaction between the nanoparticles and the surfaces of the fungi, they have observed similar phenomena from other common filamentous fungi and actinomycetes. Using these species, the researchers have produced tube-shaped structures up to tens of micrometers long with diameters ranging from 0.8 μm to 12μm.

MAXIM NIKIFOROV

Influence of Icosahedral Short-Range Order in Undercooled Melts on the Nucleation Barrier Directly Observed

More than 50 years ago, F.C. Frank hypothesized that undercooled liquids may contain icosahedral short-range order (ISRO), which would be incompatible with the long-range order of the crystalline phase, thus creating an energetic barrier for crystallization. Up to now, however, the hypothesis had not been confirmed by direct experimental observation. K.F. Kelton of Washington University, R.W. Hyers of the University of Massachusetts—Amherst, T.J. Rathz of NASA Marshall Space Flight Center, D.S. Robinson of Ames Laboratory, and co-workers have reported in the May 16 issue of *Physical*

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Review Letters direct experimental proof of the hypothesis. They used x-ray scattering to study a deeply undercooled TiZrNi liquid to demonstrate the correlation between the nucleation barrier and growing ISRO with decreasing temperature. Beamline electrostatic levitation (BESL), a technique recently developed by Kelton, made the experiments possible, allowing *in situ* x-ray diffraction studies on electrostatically levitated droplets.

The researchers used containerless processing to study 2.3–2.5-mm-diameter TiZrNi droplets, which were melted using a YAG laser and charged positively by using ultraviolet light followed by levitation in vacuum (10^{-7} Torr) between electrostatic plates. Decoupling between heating and positioning using electrostatic levitation showed an improvement over electromagnetic levitation techniques, allowing undercooling studies on a wider range of materials.

In the case of the TiZrNi system investigated, the researchers found that the increasing ISRO is responsible for the nucleation of the metastable icosahedral *i*-phase formed in the first of two recalescence events (a 105 K temperature rise), instead of the thermodynamically stable polytetrahedral C14 Laves phase, which forms just a few seconds later, recognized by a second recalescence (a 25 K temperature rise). Recalescence is the process whereby the liberated heat of fusion causes a temperature rise during solidification. Since the driving free energy for the formation of the C14 phase is larger, the preferred nucleation of the *i*-phase indicates a smaller nucleation barrier, consistent with the x-ray evidence that the short-range order in the supercooled liquid is closer to that of the *i*-phase than to that of the C14 structure.

A better understanding of the physics of undercooled liquids is of technological importance, particularly the elucidation of the reasons for the unusual stability of undercooled liquids against crystallization in order to gain better control of their nucleation behavior. Commercial interests lie in the manufacture of glass fibers from undercooled oxide melts, making accessible novel fibers for structural, optical, and medical applications as well as oxide glasses for infrared and laser applications in telecommunications and consolidated nanostructured metallic glasses.

ALFRED A. ZINN

Geometry Can Provide Interlocking of Protective Tiles for the Space Shuttle

One of the critical components on the space shuttle is its thermal protection system (TPS). The TPS consists of various materials applied externally, primarily in the form of tiles, to the outer structural skin of aluminum and graphite epoxy. During reentry of the shuttle from earth orbit, the TPS protects the skin from overheating and failure due to the frictional heating of high-speed contact with the earth's atmosphere.

A weakness of the TPS is that mechanically it is not a cohesive system. Each of the tiles is an independent unit, and damage to or failure of one tile can cascade into overall catastrophic failure. Yuri Estrin (Technical University of Clausthal, Germany) along with A.V. Dyskin, E. Pasternak, H.C. Khor from the University of Western Australia and A.J. Kanel-Belov from the International University of Bremen, Germany have proposed a new concept for the design of the tile-covering, based on topological interlocking of the tiles.

The basis of their proposal, as published in the June issue of *Philosophical Magazine Letters*, is the idea of geometrically subdividing a continuous layer into fragments that are topologically interlocked. One example of this for a planar plate is the "osteomorphic block," which includes a class of shapes that allow for masonry-like assemblies. The contacting surfaces are curved such that the concave surface of one element meshes with the convex surface of a neighboring element, resulting in interlocking. Since the interlocking is independent of the material and block dimensions, it is possible to use different materials and varying dimensions, so long as they fit into a cohesive whole. In the case of the space shuttle, most of its surfaces are nonplanar, and the thermal cladding will require the use of nonplanar osteomorphic blocks (tiles).

One major advantage of the interlocking structure is that even if individual tiles are cracked or damaged, they will still be held in place by neighboring tiles. Thermal expansion of the tiles can be accommodated by the inclusion of gaps between the tiles, provided that the gaps are small and do not affect the interlocking.

The recent tragic loss of the Space Shuttle Columbia and its crew of seven astronauts underlines the safety concerns of every system that makes up the spacecraft. There is strong evidence that a piece of foam from one of the booster rockets struck and damaged the carbon-fiber composite panel on the edge of the left wing of the shuttle (part of the TPS not protected by tiles). Although topologically interlocked tiles might not prevent similar disasters in future spacecraft, they may form a safer TPS for the parts of the spacecraft where tiles are used.

GOPAL R. RAO

Shock-Wave Modulation of the Dielectric Constant of Photonic Crystals Produces Optical Phenomena

Dielectric photonic crystals are opening promising new methods to control the propagation of light. E. Reed, M. Soljacic, and J. Joanapoulous of the Massachusetts Institute of Technology, through numerical simulations and analytical theory, have explored the phenomena associated with light scattering from a shocklike wave in a photonic crystal. They have uncovered three phenomena, which they reported in the May 23 issue of *Physical Review Letters*. The first is the transfer of light frequency from the bottom of a bandgap to the top (up-conversion) or vice versa (down-conversion). The second is the capture of light of significant bandwidth in a localized region at the shock front for a controlled period of time. And the third is the possibility of achieving a decrease in the bandwidth of the propagating light. The researchers reported that when light is captured at the shock front, it is possible to observe reemission at a tunable pulse rate, and at a tunable frequency with a narrowing bandwidth.

The researchers said that shocked photonic crystals can be an alternative to nonlinear materials for frequency switching, and they also can be powerful materials for the manipulation of light pulses for quantum information. In their analysis, for illustrative purposes, the researchers modeled their photonic crystals with a part containing the shock wave and an unshocked part. They assumed that the period of the shocked crystal is half of that of the original crystals and that the shock wave moves into the unshocked part of the crystal at a given velocity. They describe the computed time-dependent optical phenomena in terms of the changes in time of the numbers of unit cells in each part of the crystal. For practical purposes, they considered the effect on a photonic crystal, for example a silicon/silicon dioxide multilayer, shocked to a strain of a few percent. From their analysis, the researchers find that shining light into this crystal will result in reflected light with a frequency shift of the order of 1%, a pulse rate of 10 GHz for light of