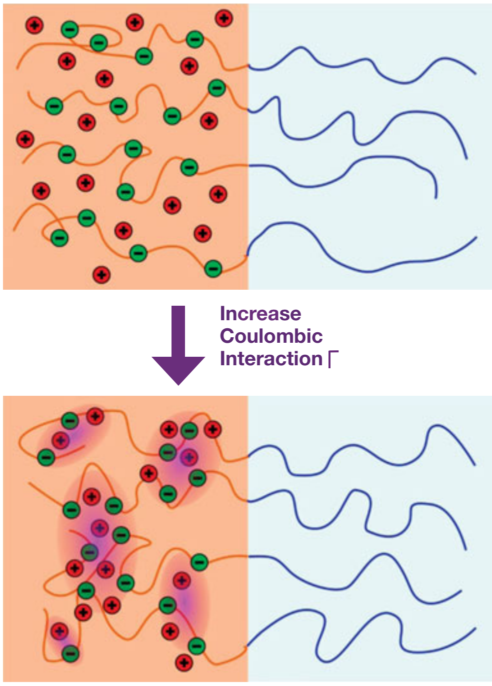
Nano Focus

Electrostatic control achieved in block copolymers through morphology

The development of energy conversion and storage devices is at the forefront of research geared toward a sustainable future. However, materials limitations serve as bottlenecks in this progress. Typical liquid electrolytes used for the transport of ions between an anode and cathode are highly flammable and pose a safety hazard. Research efforts have focused on exploring solid electrolytes that do not have these limitations. Block copolymers are an alternative as solid electrolytes because they can self-assemble into nanostructures, which enables ion transport and maintains structural integrity. Furthermore, the ion conductivity can be controlled according to the nanostructure geometry.

Researchers Charles E. Sing, Jos W. Zwanikken, and Monica Olivera de la Cruz from Northwestern University have used a theoretical model to demonstrate that the distribution of charge on the blocks comprising block copolymer systems can be used to manipulate the copolymer through inducement of an array of nanostructures. As reported in the July issue of *Nature Materials* (DOI: 10.1038/NMAT4001; p. 694), the researchers varied the charge density along the block copolymer backbone through straightforward design of parameters. Charges along one of the blocks as well as the corresponding counterions dictate the equilibrium properties of the block copolymers through a combination of entropy, ion solubility, and electrostatic cohesion, which taken together drastically manipulate the phase behavior. The accompanying figure depicts the effect of charge cohesion on nanostructure phase behavior, demonstrating that highly asymmetric charge cohesion effects can induce the formation of nanostructures that are inaccessible to conventional uncharged block copolymers, including percolated phases desired for ion transport.



Effect of charge cohesion on nanostructure phase behavior showing electrostatic cohesion between the charged A-blocks and the counterions. When the interactions are strong, the components are electrostatically correlated in a liquid-like ordered structure, which has a significant effect on the phase diagram. Reproduced with permission from *Nat. Mater*. **13** (2014), DOI: 10.1038/nmat4001. © 2014 Macmillan Publishers Ltd.

This work presents an orthogonal route toward tuning nanostructures that will have a significant impact on the design of block copolymer materials for use in numerous applications, such as in lithographic templates for small electronics, sensors, drug delivery, vehicle filtration membranes, and materials with novel and tunable mechanical properties.

Jean L. Njoroge

Mechanical metamaterials produce ultralight, ultrastiff lattices

The word "metamaterial" conjures up visions of matter interacting with electromagnetic waves to bend the waves around objects, producing a "cloaking device" that hides the object from detection. But the "mechanical metamaterials" that Chris Spadaccini's group at Lawrence Livermore National Laboratory and Nicholas Fang's team at the Massachusetts Institute of Technology (MIT) are working on aim to avoid bending as much as possible—mechanical bending, that is. Instead, by causing forces to distribute only in stretching or compression modes along the struts of an octet truss, they have fabricated ultralight, ultrastiff materials from polymers, metals, and ceramics. These materials could have applications in automobiles and aircraft, among other applications, where lightweighting could help conserve fuel without giving up strength.

"I don't know who coined the term 'mechanical metamaterial' or 'structural metamaterial,'" Spadaccini said, "but we think it's appropriate in that a metamaterial is something that has a unique property that is based on the structure and the layout of the material as opposed to its composition."

The unique properties of what Spadaccini calls their "architected" material combine the lightness of an aerogel with a stiffness that is four orders of magnitude higher than that of a typical aerogel. The stiffness and density scale linearly over this range of magnitudes. In cellular materials found in nature, the scaling factor is usually a power of two (quadratic) or three (cubic) or higher, leading to deleterious nonlinear effects that result in a dramatic loss of stiffness with decreasing density. Natural materials tend to have more random pore sizes and distributions that lead to bending under stress.

"You really need to have more of those members within your material that are stretching or in compression as opposed to bending in order to move off that cubic relationship," Spadaccini said. "But there

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aren't many geometric configurations that you can conceive of where nearly all of the elements are in either tension or compression."

In this case, the researchers chose one of the known geometric configurations that satisfies this requirement, the octet truss, for their experiments, as reported in the June 20 issue of *Science* (DOI: 10.1126/science.1252291; p. 1373). The unit cell of the octet truss has a regular octahedron at its core, with eight regular tetrahedra on its faces, which lead to a face-centered-cubic (fcc) structure. Using projection microstereolithography, they were able to produce highly ordered, nearly isotropic microlattices within these fcc, stretch-dominated architectures. Critical features in the 20 µm to 40 nm range created lots of void space for ultralightweight properties.

One key to their success was the ability to use projection microstereolithography to fabricate arbitrary, three-dimensional (3D) microscale structures. This additive manufacturing technique is based on building patterns of photocured polymer resins (HDDA or PEGDA) layer by layer. The pattern is generated slice by slice from a 3D CAD model, and projected through a liquid-crystal-on-silicon chip, which acts as a reconfigurable digital photomask, onto the surface of a bath of UV-curable resin. After a layer hardens, the sample is lowered in the polymer bath, new resin coats the surface, and the next layer of the 3D structure is projected and polymerized onto the layer beneath.

The result is an extended microlattice of octet truss unit cells made of solid polymer struts. By coating these struts with a nickel-phosphorus alloy through electroless nickel plating, and removing the polymer struts through thermal decomposition, a hollow-tube metallic Ni-P microlattice can be formed. Similarly, by depositing the ceramic Al_2O_3 by atomic layer deposition onto the polymer struts and removing the polymer, a hollow ceramic Al_2O_3 microlattice is formed. For yet another configuration, Al_2O_3 nanopowder is mixed in with the polymer before the process begins, resulting in a structure consisting of a polymer–ceramic hybrid core. Subsequent heat treatment decomposes the polymer and sinters the Al_2O_3 to form a solid ceramic microlattice.

In each case (polymer, metallic, hollow ceramic, solid ceramic), uniaxial compression studies yielded plots of relative compressive stiffness and relative compressive strength versus relative density. These plots showed the stiffness and strength to be linear functions of the relative density of the material for each of these stretch-dominated lattices. In contrast, a bend-dominated, solid polymer Kelvin foam made by the same process for comparison decreased in strength and stiffness by a power of two with decreasing density.

"We fabricated an ultrastiff, ultrastrong material that is primarily void space, which makes it very light weight," Spadaccini said. "Then we took that a step further by combining additive micromanufacturing processes with nanoscale coating processes to give us a material that is about as light as an aerogel. The mechanical properties, relative to the material's density, go through the roof."

Tim Palucka

Fast electronic switching of ultrathin films of phase-change materials render nonvolatile color changes

Phase-change materials (PCMs) switch between amorphous and crystalline solid states. The process can occur at ultrahigh speeds (on the order of MHz), and may be driven thermally, optically, or electrically. Controlling the associated changes in the PCM's optoelectronic properties is a great motivator to investigate and characterize such systems. As reported in the July 10 issue of *Nature* (DOI: 10.1038/nature13487; p. 206), Peiman Hosseini and Harish Bhaskaran at the University of Oxford and C. David Wright at the University of Exeter induced phase switching within sputtered $Ge_2Sb_2Te_5$ (GST) films. These phase changes take place within low-dimensional nanoscale-sized regions, and the optical properties (e.g., color) in these regions change in a reversible, stable manner.

The researchers started by sandwiching GST between two layers of indium tin oxide (ITO), and depositing it on a reflective platinum surface. Crystallization of the GST changes its refractive index, which in turn changes the color of the multilayered stack when illuminated with "white" light. No energy is required after a switching event to maintain the new color, which is a distinct advantage in low-power display applications. In short, the group demonstrated the principle behind a PCM-based, nonvolatile reflective display.

The researchers modeled the stack using a transfer matrix optical computational method, and calculated optoelectronic properties such as color, reflectance, internal electric field, and transmittance. The model simulates the stack's optical properties for GST in its as-sputtered amorphous state, and also in its crystalline state. Hosseini and colleagues found excellent agreement between their model data and the experimentally measured reflectivity spectra of the films.

The researchers next turned their attention to how the thickness of each of the three films affects the properties of the overall stack. They confirmed a strong dependence of color on film thicknesses. Furthermore, smaller GST thickness enhanced the reflectivity contrast between the amorphous and crystalline states, and fortuitously for display applications, required less power to switch. The researchers also tailored the thickness of the ITO layers to enhance the reflectivity of specific wavelengths; in effect, they demonstrated that it is possible to create a pixel of a specific color for a reflective display.

Working both with a continuous ITO/GST/ITO/Pt film and a similar film with lithographically defined pixels, they used the conductive tip of an atomic

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