



the regions of hydrogenated graphene, which are termed graphane; see (a) in the figure. Partial hydrogenation of the graphene was confirmed using Raman spectroscopy. Measurement of the electronic properties of this material using four-probe analysis demonstrated a gradual transformation from semimetallic graphene to a near insulating graphane-like material with increasing hydrogenation.

The researchers also further functionalized the graphene/graphane superlattice with 4-bromophenyldiazonium tetrafluoroborate. They proposed that

spontaneous electron transfer occurs from the graphane to the diazonium salt, generating an aryl radical that attacks the sp^3 C–H bonds to form new, covalent sp^3 C–C bonds; see (b) in the figure. Transmission electron microscopy and electron diffraction patterns of the diazonium functionalized films confirmed that the graphene structure survives the functionalization reactions. The extent of diazonium functionality was investigated using x-ray photoelectron spectroscopy, which showed that functionalized films containing as much as one new sp^3 C–C

bond for every 21.5 C atoms in the graphene domains could be achieved using this methodology.

The researchers said that their “two-step controlled covalent functionalization process permits modulation of the electronic properties of graphene’s basal planes and could hold promise for specifically patterned optoelectronic and sensor devices based on this exciting new material.”

Steven Trohalaki

Bio Focus

Self-assembled curved 3D structures with integrated microfluidic network achieved by differential cross-linking of polymer thin films

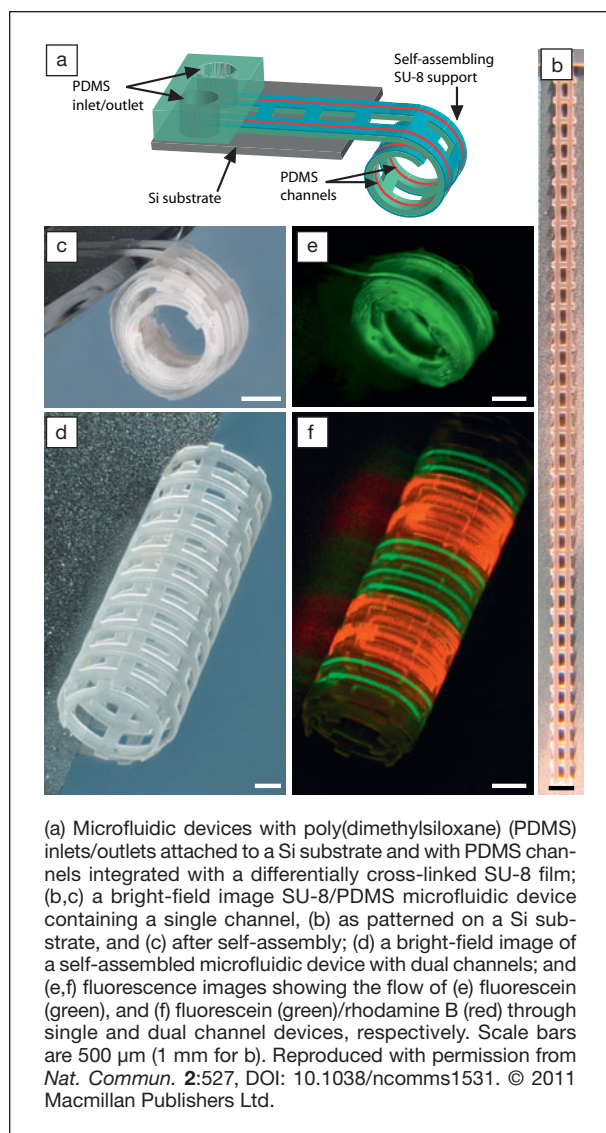
Materials with three-dimensional (3D) curved structures that contain embedded microfluidic channels are of great interest, providing mimics of natural structures such as leaves and tissues. These are permeated with vasculature systems to enable the efficient local transport of nutrients and waste products. Although self-assembly to 3D geometries can be obtained by introducing structural and mechanical heterogeneity in a material, integrating this with a microfluidic network to enable precise delivery of fluid in curved locations, or to create 3D vasculature, creates significant challenges. Recently, D.H. Gracias and colleagues from John Hopkins University have created such a self-assembled microfluidic network by integrating poly(dimethylsiloxane) (PDMS) channels in differentially photo-cross-linked SU-8 (a negative photoresist) thin films which spontaneously and reversibly curve on desolvation and resolvation.

As reported in the November 8, 2011 issue of *Nature Communications* (DOI: 10.1038/ncomms1531), the researchers first created heterogeneous SU-8 films with crosslink gradients (CLGs) along their thickness by exposing the films to

ultraviolet (UV) light. The films were then soaked in acetone to condition them and to generate stress gradients for self-assembly. The SU-8 films then spontaneously curved on desolvation by drying or the addition of water and then re-flattened when resolvated by organic solvents like acetone.

The radii of curvature strongly depend on UV exposure energy and the film thickness and a wide range of geometries could be obtained by simply varying the CLG using conventional photolithography.

The ability of these SU-8 templates to show reversible curvature could also be exploited to curve thicker polymeric films deposited on the surface of a prepared SU-8 film. Integration of microfluidic channels into the polymer film surface layer then enabled the construction of a curved microfluidic device. Fluid flow through the networks with single and dual channel devices established the functionality of the devices as a pathway for fluid transport to curved locations (see Figure).



(a) Microfluidic devices with poly(dimethylsiloxane) (PDMS) inlets/outlets attached to a Si substrate and with PDMS channels integrated with a differentially cross-linked SU-8 film; (b,c) a bright-field image SU-8/PDMS microfluidic device containing a single channel, (b) as patterned on a Si substrate, and (c) after self-assembly; (d) a bright-field image of a self-assembled microfluidic device with dual channels; and (e,f) fluorescence images showing the flow of (e) fluorescein (green), and (f) fluorescein (green)/rhodamine B (red) through single and dual channel devices, respectively. Scale bars are 500 μm (1 mm for b). Reproduced with permission from *Nat. Commun.* 2:527, DOI: 10.1038/ncomms1531. © 2011 Macmillan Publishers Ltd.

The SU-8/PDMS devices are bio-inert and remain curved in culture media.



They can therefore be used in biological applications to transport biochemical nutrients or growth factors for tissue engineering. Incorporation of litho-

graphically defined pores can also be used to locally release chemicals. The researchers also created a reconfigurable metamaterial suggesting that these self-

assembling devices could prove useful as 3D electromagnetic devices.

Mousumi Mani Biswas

Nano Focus

Hollow spacers lead to new possibilities in superlattice design

Highly ordered arrays of nanoparticles hold the promise of functionality determined by the periodic arrangement of their constituent nanoscale building blocks. The rational assembly of DNA-functionalized nanoparticles has proven an effective method for generating well-defined crystalline lattices, but is limited in the number of geometries. C.A. Mirkin, E. Auyeung, J.I. Cutler, and their colleagues at Northwestern University have recently improved the capabilities of this method, allowing them to create lattices with previously unobserved symmetries. As reported in the January issue of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2011.222; p. 24), Mirkin's group demonstrates the utility of three-dimensional hollow spacers, or spherical nucleic acid (SNA) nanostructures, that take the place of DNA-functionalized gold nanoparticles, enabling the researchers to expand the library of superlattices they are able to create as well as to make novel structures not previously observed in nature.

The hollow spacers are made using gold nanoparticles as a template and offer the potential of superior control over the superlattice structure. The technique utilizes gold nanoparticles functionalized with alkyne-modified DNA, which can be employed to generate a rigid network by cross-linking the densely packed alkyne units. The gold particle cores within the DNA shells are then dissolved, generating hollow spherical nucleic acids (SNAs) nanoparticle conjugates which are nearly identical in size to their gold nanoparticle counterparts. They also exhibit many of the same unique chemical and physical properties, including the ability to participate in cooperative binding events, which is a necessary requirement for their use in this programmed assembly application. However, the spacers do not scatter x-rays and are observed as blank positions in x-ray scattering experiments.

The research team demonstrates the utility of hollow SNA nanostructures by first changing the molar ratio of the gold nanoparticle units to spacer particles, and secondly by changing the size of the gold and spacer nanoparticles. Initially, a body centered cubic (bcc) system was formed using two sets of gold

nanoparticles of equal size (molar ratio 1:1) and with complementary sticky ends (5'-AAGGAA-3' for the first group and 5'-TTCCTT-3' for the second group). By replacing one of the gold nanoparticle groups with a hollow spacer group, the researchers were able to form a simple cubic system.

Alternatively, a 2:1 ratio of 20 nm and 10 nm gold nanoparticles was used to create AB₂-type crystal superlattices. By substituting the gold nanoparticles in this system for spacers, the researchers demonstrated simple hexagonal (10 nm spacer) and graphite-like symmetries (20 nm spacer). Finally, AB₆ symmetry was created using a 1:6 ratio of 20 nm to 10 nm gold nanoparticles. When the 20 nm spacer was substituted for 20 nm gold nanoparticles, a completely new symmetry group was observed that the team dubbed "Lattice X."

The researchers said that the improved structural diversity provided by their hollow particle approach will lead to the development of new functional materials that can be used in a wide variety of applications ranging from plasmonics to catalysis.

Kevin P. Herlihy

Hydrogen at room temperature is squeezed to become a metal

Hydrogen, one of the most basic and well-studied elements, still has surprises in store. At pressures exceeding several million atmospheres, hydrogen is predicted to become metallic, superconducting, and may even exhibit superfluidity.

In the November 13, 2011 online edition of *Nature Materials* (DOI: 10.1038/NMAT3175), M.I. Erements and

I.A. Troyan at the Max Planck Institute for Chemistry describe experiments in which molecular hydrogen undergoes transformation to dense hydrogen and then a conductive, metallic state under the megabar pressures exerted by a diamond anvil cell (DAC).

The hydrogen sample first becomes opaque at a pressure of about 220 GPa, and is a semiconductor, as shown by photoconductivity measurements where the samples conduct on illumination with a He-Ne laser (photon energy of 1.96 eV). As the pressure is increased, the width of

the bandgap decreases, and the samples can conduct without illumination. Finally, the bandgap closes at an applied pressure of about 270 GPa. Erements and Troyan propose that a first-order phase transformation to a metallic, monatomic liquid state occurs at that pressure, since the resistance drops precipitously and exhibits little pressure dependence at higher applied pressures. This metallic state was confirmed by cooling the sample down to about 30 K, and noting that the resistance remained low (in contrast with a nonmetal, which insulates at sufficiently