

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



low temperatures, because charge carriers cannot be thermally excited across the bandgap). Further proof was obtained from the presence of significant hysteresis in the structure/pressure relationship. On reducing the applied pressure below 270 GPa, a back transformation to molecular hydrogen takes place at about 200 GPa.

Previous DAC experiments have been carried out at low temperatures (~100 K) to mitigate the hydrogen diffusing into and ultimately destroying the diamonds. The current experiments were performed

at room temperature (295 K) by covering the diamond culets with diffusion barriers consisting of ultrathin layers of Cu, Au, or alumina. These semitransparent layers also enabled structural changes in the hydrogen to be studied using optical techniques, and Raman spectroscopy confirmed that molecular hydrogen becomes opaque and conducting under pressure and that it ultimately transforms into a monatomic liquid. Troyan and Eremets also noted that new Raman bands appeared in the 220–270 GPa range, which

suggests either that the hydrogen retains its Phase I structure until it transforms to a metallic monatomic liquid state, or that it transitions to another phase at 220 GPa.

“Our results on the transformation of normal molecular hydrogen at room temperature to a conductive and metallic state,” said the researchers, “open the door to more comprehensive studies of metallic hydrogen, and further understanding of hydrogen’s phase diagram.”

Rich Louie

Bio Focus

High-resolution mapping of soft surface chemistry achieved

Noncovalent interactions between soft materials in solution are an essential component of processes such as biodetection and catalysis, and for the development of technologies including microfabricated devices. Despite this, imaging surface interactions remains highly challenging. One recently developed strategy has used the distribution of fluorescent molecular probes on a surface to build a picture of relative changes in chemical topography. In the November 1, 2011 issue of *Nature Communications* (DOI: 10.1038/ncomms1530), R. Walder and colleagues from the University of

Colorado have taken this approach a step further to produce high-resolution maps of the noncovalent chemistry of soft surfaces, using data from the whole surface trajectory of absorbed molecules.

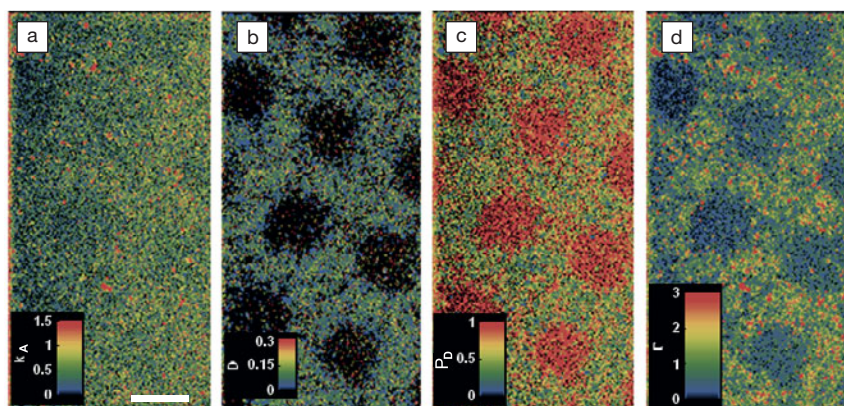
This work uses self-assembled monolayers of trimethylsilane on fused silica as substrates, as these hydrophobic surfaces can be easily micropatterned with hydrophilic regions by exposure to UV light through a suitable mask. Fatty acid molecules that were labeled with the boron-dipyrromethene (BODIPY) fluorophore were chosen as suitable probes, and were applied to the surface in a dilute solution. Each absorbed molecule could then be distinguished using total internal reflection fluorescence microscopy. By taking a series of these snap-

shots over a period of several minutes, the individual trajectories of the probe molecules over the surface could be tracked. A high throughput analysis of these time-resolved images then allowed real dynamic parameters such as absorption rate, diffusion coefficient, and surface occupancy at each surface pixel to be extracted, and maps of the variation of each parameter to be produced (see Figure).

Each of these maps was able to clearly resolve grids of 10 μm hydrophilic squares where affinity with the fatty acid is much lower than on hydrophobic areas. Further, calibration measurements on a series of homogeneous surfaces with different hydrophobicity demonstrated that single-molecule interactions can be used to probe local hydrophobicity quantitatively on an absolute scale.

The team dubs this new imaging technique “mapping using accumulated probe trajectories” or MAPT and, like other molecular probe methods, its resolution is not diffraction limited. While 125-nm features were resolved in this demonstration, its limits are closely tied to the specific interaction between the probe molecule and the surface. Through appropriate choice of probe molecule, it should be possible to extend the technique beyond hydrophobic interactions to mapping variation in surface reaction rates or conformational changes in surface proteins.

Tobias Lockwood



Mapping using accumulated probe trajectory (MAPT) images of (a) adsorption rate, k_A ($10^{13} \mu\text{m}^{-2}\text{s}^{-1}\text{M}^{-1}$) (scale bar is 10 μm); (b) average diffusion coefficient, D ($\mu\text{m}^2/\text{s}$); (c) desorption probability per 400 ms, P_D ; and (d) surface coverage/occupancy, Γ ($10^{13} \mu\text{m}^{-2}\text{s}^{-1}\text{M}^{-1}$) on a photo-patterned trimethylsilane surface. Reproduced with permission from *Nat. Commun.* 2:515, DOI: 10.1038/ncomms1530. © 2011 Macmillan Publishers Ltd.