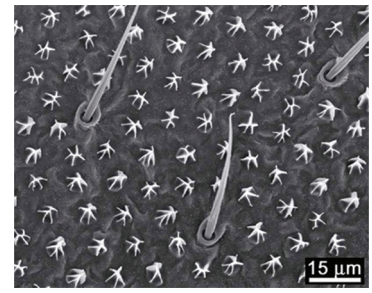
Like Water off a Termite's Wing

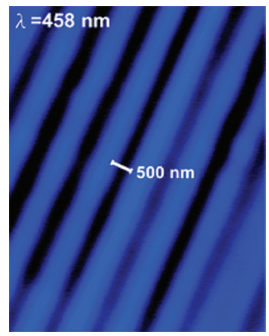
The pharmaceutical industry has long looked to nature as a source of design for its products, and now nanotechnology is looking at naturally occurring nanostructures for design inspiration. In particular, the nonwetting surfaces found on terrestrial insects could guide the development of surfaces with antiwetting properties. One such superhydrophobic surface is found on the wings of termites. Though termites are weak fliers, they are known to fly during rainy periods, and water droplets placed on termites' wings spontaneously roll off the surface.

To investigate the superhydrophobic nature of termite wings, Watson *et al.* (p 129) used optical images of water droplets on the wings of two species of termites to identify hairs that suspended the droplets above the wing surface membranes. Scanning electron microscopy showed that the hairs have deep troughs that extend along the long axis of the shaft. Coating these hairs with a thin layer of hydrophobic polymer did little to affect their droplet-suspending capabilities. However, coating the hairs with a thick layer of polymer, which obscures the troughs, rendered the hairs unable to hold up droplets, suggesting that the troughs' architecture is largely responsible for repelling water. Further, the researchers found that an array of star-shaped structures, called micrasters, appear to catch droplets of water small enough to fit between the hairs and prevent them from touching the wing surface. The researchers suggest that this new understanding of termite wings' nonwetting surfaces may eventually contribute to the next generation of bioinspired nanomaterials.



Data Storage Goes Gold

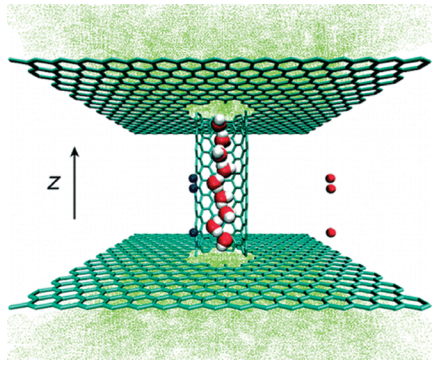
Metal nanoparticles are appealing to researchers for numerous fundamental and technological applications, including their surface plasmon resonance (SPR) properties. The SPR wavelengths of hollow gold nanoparticles (HGN) are known to be readily tunable into the near-infrared region, which may be useful for surface-enhanced Raman scattering (SERS), optical imaging, and chemical sensing. However, little is known about the effect of pulsed-laser irradiation in non-SPR absorbance regions, especially the deep-ultraviolet (DUV) region. If HGNs responded similarly to such shorter wavelengths, it could be a boon to optical data storage, with shorter laser wavelengths causing resolution and thus data density to be significantly enhanced.



In a new study, Wan *et al.* (p 165) tested the effect of a one-shot KrF laser on HGNs affixed to various surfaces, including glass slides, silicon wafers, and flexible plates and tapes. The researchers employed a range spectroscopic and imaging methods to investigate changes in the optical properties and morphologies of the HGNs induced by irradiation from the laser. Results showed that the KrF laser effectively melted the HGNs into smaller nanoparticles, leading to blue shifts of the SPR peak. They further showed that these HGN-coated surfaces have the ability to be patterned with submicrometer resolution through a phase mask. The researchers propose that these patterns could be used as a readout when using a blue-ray transmission laser microscope. If flexible substrates such as a HGN-coated tape are used, they speculate, data density could increase to hundreds or thousands of times higher than current optical data storage methods allow.

In Nanotubes, Water Goes with the Biomimetic Flow

Elucidating the details of water movement inside hydrophobic carbon nanotube (CNT) channels could have implications for applications including hydroelectric power converters, desalination of seawater, and drug delivery. To this end, researchers have devoted considerable attention to bidirectional single-file water transport in both plain and chemically modified CNTs to serve as prototypes for biological water channels. Recently, investigators proposed a concept for a molecular water pump, with three charges asymmetrically positioned adjacent to a CNT, an idea inspired by the charge distribution in biological water channels called aquaporins. Their molecular dynamic simulations showed a unique unidirectional flow resulting from an asymmetrical water-charge potential between two ends of the tube, suggesting a new way to design controllable nanofluidic devices. However, since aquaporins conduct water passively in response to an osmotic gradient but cannot act as unidirectional pumps, questions remain as to the feasibility of this device.



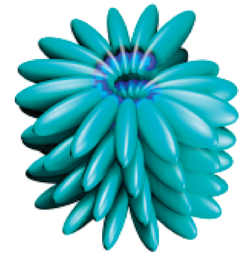
To investigate whether such an efficient, unidirectional pump can be achieved, Zuo *et al.* (p 205) developed a biomimetic water channel consisting of a (6,6) CNT embedded between two graphite sheets solvated by bulk water. They positioned three positive charges along the *z* axis and three corresponding negative countercharges to keep the system electrically neutral. Their molecular dynamic simulations point to different conclusions than previous studies, namely that cumulative flux of the water molecules through this system is nonlinear, with flow direction varying frequently with increasing simulation time. Energetic analysis suggests that the water−water interactions, determined by dipole orientation configuration, significantly influence the transport rate. They suggest that these findings could yield new insights for developing more efficient nanofluidic devices.

Published online January 26, 2010.
10.1021/nn901891y

The Making of a Virus

Like most biological macromolecules, viral capsids form through self-assembly of molecular building blocks, multiple copies of protein monomers or oligomers. The majority of capsids are spheroidal with icosahedral symmetry, but a wide variety of nonspherical shapes are also known, including the conical HIV virus. The factors that promote viral shape have not been fully elucidated. Although it is known that the shape of the building blocks directly influences the overall shape of the assembled structure, the way in which it does so is not understood well enough to allow for efficient bottom-up design of these nanostructures.

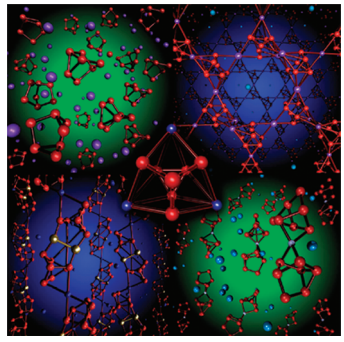
Seeking the mechanism behind capsid assembly into various shapes, Fejer *et al.* (p 219) developed a simple, generic model that contains all the features necessary for self-assembly into a wide variety of shapes found in nature, including spherical, tubular, helical, and head−tail structures. Their model, which relies on anisotropic building blocks, suggests that nonspherical shells appear spontaneously whenever the number of particles is insufficient or incommensurate with a highly symmetric shell, this being the most efficient way to maximize favorable contacts



while minimizing interparticle repulsion. The researchers found that the anisotropy of the building blocks systematically determines the preferred geometry of the dimer, which in turn defines the morphology of larger clusters. They extrapolate these results to various capsid structures found experimentally, including two-layered structures. The authors suggest that the structural trends derived from their model can be used as a starting point for the rational design of nanoscale assemblies with selected shapes.

Cluster-Assembled Materials Mind the Band Gap

Cluster-assembled materials serve as a link between the predictable properties of solids and the variation in physical and electronic properties observed at the subnanometer scale. The chemical, electronic, and magnetic properties of clusters vary with size and composition, due to quantum confinement and chemical interactions; as such, cluster-assembled materials could find use as controllable band gap materials. However, the factors controlling the properties of materials once clusters have been incorporated into larger assemblies are unknown. Though previous research has suggested that countercations play an important role in determining the electronic structure of these materials, no direct correlations between theoretical calculations based on actual crystal structures and empirical band gaps have been reported.



To bridge this disparity, Qian *et al.* (p 235) synthesized and characterized a range of As_7^{3-}-based Zintl cluster assemblies with different countercations. These clusters were crystallized in the presence of the polycyclic multidentate ligand cryptand-222 ("crypt"), which has a selective sequestering ability for K^+ and Rb^+ over Cs^+. Results showed that the variations in architectures and compositions of the various assemblies led to systematic differences in their electronic and optical properties. The researchers found significant variations ranging from 1.1 to 2.1 eV in the band gaps of different cluster-assembled materials made from the same As_7-cluster building block. Theoretical studies suggest this variation results from altering the lowest unoccupied molecular orbital levels by changing the countercations. This idea was tested further using linkers with less charge transfer and more covalent interactions. The researchers suggest that using this strategy to develop tunable band gap materials may eventually find applications in optoelectronics and enable the assembly of materials with multiple band gaps.

Multiple Nanoscale Templates from a Chip off the Old Block Copolymer

Researchers are increasingly interested in the self-assembly of block copolymers as promising platforms for the bottom-up fabrication of nanostructured materials and devices. The molecular characteristics of the component block copolymers dictate this self-assembly process, and thus are critical in the formation of lithographic templates by controlled degradation. The growing focus on block copolymer lithography in the fabrication of nanomaterials has led to a new challenge in the creation of low symmetry, nontraditional arrays of patterned nanostructures, such as rectilinear or square arrays. While these formations are more desirable than more standard geometries, they are energetically less favorable, making their production using a purely covalent diblock copolymer system impractical.

Seeking a way to overcome this limitation, Tang *et al.* (p 285) used an orthogonal approach. The researchers combined block copolymers that incorporate independent degradation chemistries, permitting each to be addressed sequentially. Their blend included a block copolymer containing hydrogen-bond (H-bond) donor groups and an ultraviolet (UV)-degradable domain, along with a complementary copolymer containing H-bond acceptor groups and an acid-cleavable segment. By degrading these different domains alone or in combination, the researchers produced three distinct nanoscale templates from the same starting system: cylindrical pores from one domain or the other, or a combined nanostructure with nesting arrays of both types of pores. A significant finding was that the chemically distinct nature of the blocks leads to cylindrical holes of different diameters, while the orthogonal nature of the reactions requires no specific order for degradation. The researchers note that this approach demonstrates the potential of combining orthogonal chemistry with the inherent tenability of supramolecular systems.