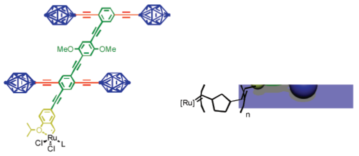
Nanocars Go for a ROMP

Devices are continuing to shrink, with their designers often seeking to mimic those on the macroscale. Among these assorted miniature devices are nanocars, which aim to transport tiny cargo with directed motion. To this end, Godoy *et al.* have created several generations of nanovehicles that are inspired by typical macrocar form, complete with chassis, axles, and molecular wheels. The first generation of these nanodevices relied on thermal activation to propel the cars on C_{60} wheels. However, thermal energy produces two-dimensional Brownian motion, not the desired unidirectional motion needed to deliver cargo purposefully.

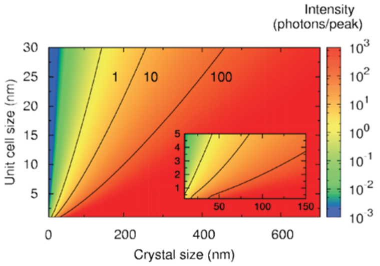
In a new study, the same team of Godoy *et al.* (p 85) crafted a new generation of nanocars that rely on a chemical energy source to drive with unidirectional motion. These new nanovehicles, equipped with *p*-carborane wheels, were attached to one of two different Hoveyda−Grubbs metathesis catalysts through a benzylidene moiety. The researchers then tested the catalytic activity of these nanocars with the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (cod). One of the catalysts showed only low activity toward this compound, but the other showed substantial polymer growth, which could propel this nanocar forward. Because of the first catalyst's low conversion rate with cod, the researchers tested this nanocar toward ROMP with cyclic strained alkene norbornene, demonstrating a high degree of polymerization. The authors suggest that incorporating these olefin metathesis catalysts in nanocars and powering ROMP reactions with suitable fuels could lead to nanocars with chemically powered propulsion.



X-ray Pulses for Nanocrystal Imaging: Ultrashort and Sweet

For more than a century, researchers have relied on X-rays to illuminate the way to a variety of biological discoveries. However, because radiation from traditional X-ray sources can quickly destroy biological macromolecules, investigators have eagerly awaited new sources and techniques that could image these molecules before damage prevents the collection of interpretable information. Consequently, some researchers have surmised that intense and very short X-ray pulses could provide the answer, because they may pass through molecules before the radiation causes major disarrangement of the atomic and electronic configurations.

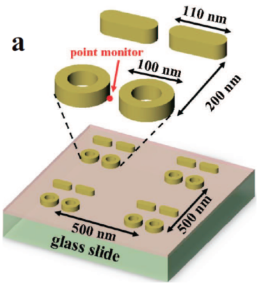
To test the feasibility of this approach, Caleman *et al.* (p 139) undertook a theoretical study of intense and ultrashort X-ray pulses on nanocrystals of urea, the organic compound found in urine. Though such crystals are typically too small to yield structural information from a conventional synchrotron source, the researchers show that such imaging could be possible using the beam from an X-ray free-electron laser. Using the example of a 1.5 Å wavelength, their simulations suggest that two ionization cascades occur simultaneously, generated by both Auger electrons and photoelectrons, and two corresponding electron clouds. They suggest that using very short pulses could limit damage by reducing both cascades and atomic disorder. They further show that using a high-intensity flux at these short pulse lengths could yield structural information for even very small crystals, while larger crystals can accommodate longer pulses at a lower intensity. On the basis of their findings, the authors suggest that these intense, ultrashort X-ray pulses could provide a much needed link between single-molecule imaging and crystallography for biological molecules.



Mixing It Up for Surface-Enhanced Raman Spectroscopy

Researchers have known for more than 30 years that the effects of Raman scattering can be enhanced by changing the texture of the substrate's surface. Since then, studies bent on finding ways to augment this effect have shown that metallic nanoparticles can play an important role. With these nanoparticles, localized surface plasmon resonances have been shown to depend on factors such as size, shape, and arrangement. Recently, a team of researchers created double resonance substrates, with plasmon resonances at both the laser excitation and Raman scattering frequencies. These substrates demonstrated significantly higher enhancement effects than single resonance structures.

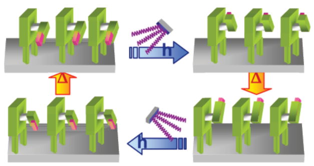
Seeking a novel way to achieve these double resonance structures, Banaee and Crozier (p 307) studied the effects of combining two gold nanoparticles with different shapes and plasmon frequencies in two-dimensional arrays. Each mixed dimer pair consisted of a rod and a ring. The researchers ran simulations comparing these mixed pairs with double dimer pairs (consisting of a rod pair and a ring pair in each unit cell), finding that both led to double resonances. The scientists then performed SERS experiments, placing benzenethiol monolayers around the exposed gold surfaces of the dimers. Results showed that SERS enhancement was significantly higher for the mixed dimers than for the double ones, with about a 4-fold larger enhancement. Further experiments involving 1,4-phenylene diisocyanide on either the mixed dimer double resonance or single resonance substrates showed that the double resonance surface showed a 3-fold enhancement. Its properties also allowed detection of Stokes lines far from the laser wavelength. The authors suggest that other nanoparticle shapes or groupings could lead to even further SERS enhancements.



10.1021/nn103468s

Tied Down: Molecular Motors on Surfaces

Biologists have long known that cells employ nanoscale motors to fulfill useful functions necessary to life. Consequently, many chemists seek to create totally synthetic molecular motors that might fulfill necessary functions in nanomachinery. Molecular motors that perform rotary motions are especially intriguing, since those in the natural world—such as bacteria flagella or the enzyme ATP synthase—are so prevalent and have proven value. To make the most out of nanosized rotary motors, confining them to a surface will be necessary to provide collective power and to minimize Brownian motion. However, little is known about how surface confinement affects various performance factors, such as rotation speed.

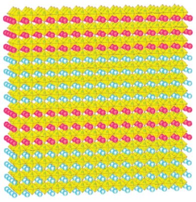


To examine this particular question, Carroll *et al.* (p 622) synthesized various light-driven rotary motors modified with either azide groups for attachment to alkyne-modified surfaces or alkyne groups for attachment to azide-modified surfaces. These motors connected to their substrates with either one or two "legs", with various tests indicating strong, covalent attachment. The researchers found that, compared to the same motors in solution, those confined to surfaces were significantly slower, with the cause being reduction in the thermal isomerization necessary for unidirectional motion. Experiments using differing amounts of surface coverage of the motors on their substrates, from 25% coverage to multiple layers, suggest that intermolecular interactions between the motors directly affect the rate of thermal isomerization. The authors note that these findings will eventually help make useful, customizable motors for assorted nanoscale machines.

Success through Strain: Detecting Nanosized Domains in Ferroelectric Superlattices

Interest has developed quickly in oxide heterostructure superlattices, a new class of ferroelectric materials with properties governed by strain and dimensionality. These materials have already been used for a variety of basic studies of size effects and coupling across interfaces. Theoretical calculations have suggested the presence of nanosized ferroelectric domains in these materials, also potentially giving them practical applications in memory storage, sensing, or switching devices. However, no experimental evidence has yet been produced to prove the presence of these domains, mainly due to the lack of a viable technique able to measure such small domain sizes.

Seeking to investigate the existence of these ferroelectric domains, Kathan-Galipeau and Bonnell (p 640) developed a novel characterization technique based on piezoelectric force microscopy (PFM), combining it with pixel-by-pixel normalization. This new technique allows picometer piezoelectric responses within the nanoscale domains to be quantified. The researchers tested this new method on thin film superlattices made of layers of $BaTiO_3$ and $SrTiO_3$. Their examination turned up nanosized domains that closely agree with those predicted by theoretical calculations. Additionally, the scientists combined information they gathered on the direction asymmetry in the domains' observed polarization with theoretical work to estimate the magnitude of the internal electric fields within the thin films. The authors note that these findings confirm the utility of their new PFM-based technique for characterizing ferroelectric domains in heterostructure superlattices. They also suggest that the protocol of combining theoretical calculations with measurements from the technique can be generalized to determine internal electric fields in other ferroelectric films.



Tapering Si Nanowires: Pointing in the Right Direction

Si nanowires that taper to a point and align vertically to a surface could be useful in applications ranging from field emitters to electromagnetic sensors. However, producing uniform arrays of Si nanowires with controlled tapering and alignment has proven to be a challenge. Researchers have had limited success using chemical vapor deposition with silane as a precursor. Though this protocol has some advantages, such as ready deposition of Si film on the nanowire sidewalls at low temperature, previous studies have shown that controlling tapering of these nanowires can be difficult. Using $SiCl_4$ is a possible alternative to silane, but the technical details necessary to produce vertically aligned nanowires with a controlled degree of taper are largely unknown.

To add to that knowledge base, Krylyuk *et al.* (p 656) systematically examined the effects of altering various growth conditions to develop an optimum method of synthesizing Si nanowires with custom tapering and a high degree of vertical alignment. The researchers found that varying the molar fractions of $SiCl_4$ and H_2 led to varying amounts of tapering, with higher ratios resulting in significantly reduced tapering but a higher percentage of vertical alignment. They also found that the gas flow rate and reactor pressure also played a part in controlling taper, with increasing flow significantly enhancing nanowire taper and low pressures leading to greater tapering and better structural quality. By varying these factors during the course of nanowire growth, they were able to create tailored tapered nanowire arrays. The authors note that their findings could lead to reliable production of tunable tapered Si nanowires and may be applicable using other precursors.