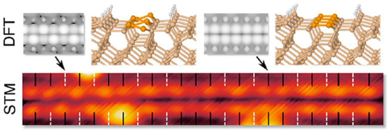
Dangling Hope for Patterning Hydrogenated Si(001)

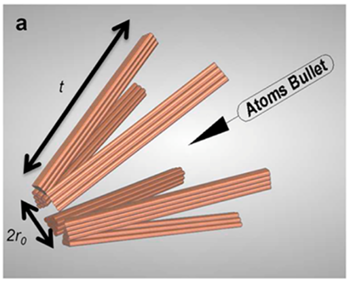
■ Some novel nanoscale structures and devices have been constructed one atom or molecule at a time using the tip of a scanning probe microscope. Although such construction is highly versatile, it is not scalable as it far too slow for real-world applications. An alternative to these painstaking atomic-scale synthetic methods is self-assembly, which has the potential to create large structures of ordered atoms and molecules, including one-dimensional chains of atoms and molecules on surfaces. However, controlling the positions, dimensions, and layouts of these chains has proven challenging. One way to influence these factors is to control the locations of chain nucleation sites on substrates. Researchers have had some success doing this on monohydride Si(001) (Si(001):H) by selectively removing hydrogen atoms with the tip of a scanning probe microscope in a process called scanning probe lithography (SPL), creating dangling bonds that are far more reactive than the surrounding hydrogen-terminated surface. However, SPL is a sequential process rather than a technique for creating long rows of dangling bonds.

In a new study, Bianco *et al.* (DOI: 10.1021/nn4010236) developed a new technique for creating those rows of dangling bonds on Si(001):H in a way that is easily scalable. By incorporating precursor Bi nanolines on the Si(001):H substrate and then hydrogenating them to remove the Bi dimers from the surface, the researchers created long rows of dangling bonds on the surface. Scanning tunneling microscopy images show that these dangling bonds manifest as both buckled dimers and flat dimers. The authors suggest that these highly reactive rows could hold promise for self-assembling new types of structures and devices.



A New Type of Nanolithography

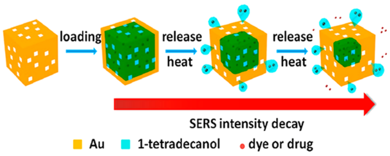
■ Nanolithography and nanofabrication methods have vastly improved over the years, with state-of-the-art technology now achieving feature sizes between 20 and 100 nm. However, to make further advances down to the few nanometer level, new approaches are needed. Some researchers have investigated the possibility of patterning surfaces using a beam of neutral atoms. Although this technique has proven successful, it has been limited to parallel lines and specific arrays because of the periodic nature of standing waves of light. Resolution has also been limited because of severe aberrations of the standing waves. Another approach uses the magnetic moments of atoms, with permanent magnets being used to focus the atoms. However, this method results in unacceptably large focal lengths.



In a new study, Castillo-Garza *et al.* (DOI: 10.1021/nn400896y) demonstrate a novel way to pattern surfaces using a pulsed magnetic lens. The researchers' scheme involves using a high-flux pulsed supersonic source to produce a small bunch of fast and cold atoms, which form a "bullet." This bullet is then divided into several bunches of atoms using a perforated pattern on a transmission mask. Finally, a lens based on a pulsed, coreless electromagnet images this pattern to a much smaller size. As proof of principle, the researchers used this technique to show the image produced by 1000 metastable Helium (He*) atoms traversing a 400-nm aperture on the mask as well as 100 He* atoms traversing an array of four 400-nm apertures. The researchers note that this technique could be used to pattern sub-10-nm structures as well as to probe surfaces as an atom microscope.

Catching Payload Release with Surface-Enhanced Raman Scattering

■ Over the past several years, researchers have pursued a variety of different nanostructures as drug delivery vehicles for targeted locoregional therapy, including supramolecular assemblies, polymer capsules, and hollow metal nanostructures. Gold nanocages (AuNCs) are particularly attractive because of their highly tunable localized surface plasmon resonance in the near-infrared, which are wavelengths that can penetrate deep into biological tissues. These particles' large scattering and absorption cross sections also make them good contrast agents for optical coherence tomography, photoacoustic imaging, and photothermal therapy. Recent research has shown that AuNCs can be effectively loaded with chemotherapeutic drugs. By incorporating "gate keeper" molecules into the cage holes, these drugs can be contained until triggered release by photothermal or ultrasonic heating. Although AuNCs have a powerful set of useful attributes for theranostic applications, they are missing a way to monitor remotely how much drug has been released, which could prove useful for physicians to determine correct dosing.



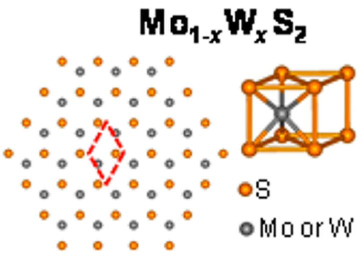
To solve this problem, Tian *et al.* (DOI: 10.1021/nn400728t) looked to surfaced-enhanced Raman scattering (SERS). Using AuNCs with a biocompatible phase-change material, 1-tetradecanol, as a "gate keeper," the researchers performed a series of tests using the dye Nile red as cargo. They showed that Raman scattering from the dye molecules is dramatically enhanced when they are in close proximity to the metal surface. When the dye is released through heating the AuNCs, Raman scattering from these molecules significantly decreases. Further tests with the Raman-active drug doxorubicin provided similar results. The findings suggest that SERS could offer a novel way to monitor drug release from AuNCs *in vivo*.

10.1021/nn402409b

Mind the Tunable Band Gap

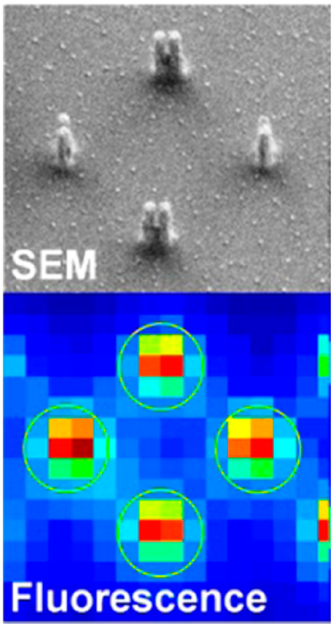
Atomically thin, two-dimensional (2D) materials have attracted growing interest because of their unique structures, interesting physical properties, and potential applications. To make the most of these intriguing materials in applications in digital electronics, optoelectronics, and elsewhere, it is essential to have a large and tunable band gap. Researchers have worked to expand the ranges of accessible band gaps in 2D materials by a variety of means, including electrical gating, functionalization, strain, and dielectric screening, with limited forward progress. Although alloying materials with different band gaps has helped to engineer band gaps in bulk semiconductors, it has been unknown whether the same strategy would work for 2D materials because no 2D alloy has yet been obtained.

In a new study, Chen *et al.* (DOI: 10.1021/nn401420h) demonstrate a family of atomically thin 2D alloys that have tunable band gaps that depend on these materials' composition. The researchers exfoliated 2D monolayers from bulk $Mo_{1-x}W_xS_2$. Scanning transmission electron microscopy images show that the arrangements of Mo and W in these monolayer alloys are random. By changing the amount of W, the researchers were able to tune the band gap of these monolayers continuously between 1.82 and 1.99 eV. The band gap of these monolayers displayed a large bowing effect, which the researchers attribute to different lowest unoccupied molecular orbital (LUMO) compositions of the two components of the alloy and LUMO bowing in $Mo_{1-x}W_xS_2$. The authors suggest that these novel atomically thin 2D alloys with tunable band gaps could lead to a variety of applications in nanoelectronics and optoelectronics.



Self-Assembled Optoplasmonic Networks Pass the Torch

Creating efficient plasmonic devices for nanoscale signal guiding, modulation, and active information processing has been limited by high dissipative losses and lack of significant electro-optical effects in metals. These limitations could be improved by optical microcavities (OM), such as dielectric microspheres, which offer whispering gallery mode resonances with long lifetimes and can efficiently trap and recycle photons. Additionally, the electromagnetic field could be significantly enhanced with plasmonic antennas. These two complementary approaches have brought on significant interest in combining both approaches into “optoplasmonic” structures. To realize the full potential of these structures, fabrication will need to integrate building blocks to couple localized surface plasmon modes with high-quality whispering gallery modes efficiently. Thus far, researchers have tried a variety of fabrication strategies, but most of these approaches are not compatible with on-chip integration into networks with defined geometries.

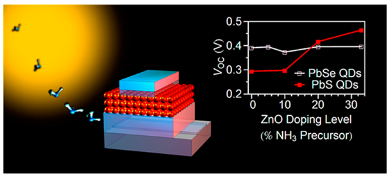


In a new study, Ahn *et al.* (DOI: 10.1021/nn401062b) demonstrate a way to self-assemble optoplasmonic molecules that efficiently transfer photons between plasmonically enhanced fluorescent dyes and OM. The researchers patterned arrays of Au nanoparticle dimers onto quartz or silicon wafers, then etched around the arrays to create Au nanoparticle-tipped nanopillars. These nanopillars were functionalized with fluorescent dye-labeled nucleotides, which served as spacers to avoid quenching of the dye fluorescence through the metal. Finally, an aqueous solution of polystyrene beads lodged beads within the nanopillar arrays. Tests showed that the fluorescent dyes preferentially emitted photons into the OM, which trapped and recirculated them with an efficiency of 44%. The authors suggest that these optoplasmonic molecules could make versatile building blocks for on-chip integrated optical networks.

Doping Metal Oxides in QD Solar Cells: The Hole Story

Semiconducting quantum dots (QDs) have increasingly been used as components in solar cells, often placed in heterojunctions with metal oxides. Thus far, research into solar cells based on QDs/metal oxides has focused mainly on the QDs, with the metal oxide receiving considerably less attention.

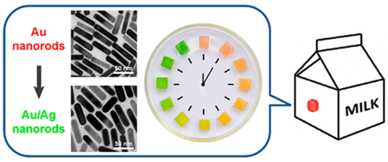
To understand the role of the metal oxides and their tunability in these devices, Ehrler *et al.* (DOI: 10.1021/nn400656n) examined colloidal QD solar cells with either doped or undoped metal oxide layers. The QDs in these devices were composed of either PbSe or PbS. The metal oxide layer, composed of ZnO, was either plain or doped with nitrogen by adding ammonia during synthesis. Although doping the metal oxide did not change device performance for solar cells using PbSe QDs, it improved the open-circuit voltage and efficiency of those using PbS QDs by 50%. This improvement was due to a reduction of carrier concentration in ZnO. The researchers used a variety of techniques to investigate the causes of this effect. Their results suggest that PbS QDs have a significant density of intragap states within the band gap. These states facilitate interfacial recombination with ZnO, which can be reduced by lowering the number of occupied states in this metal oxide. In contrast, PbSe QDs have fewer intragap states, so device performance is not limited by interfacial recombination. The authors suggest that these results stress the importance of controlling the properties of both QDs and metal oxides in solar cells.



Perishing the Thought of Spoiled Food

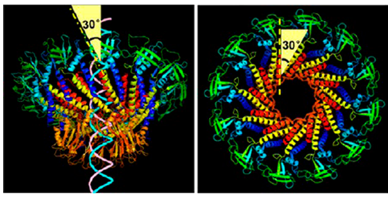
■ Perishable products, by definition, spoil over time due to microbial growth or chemical degradation. Expiration dates printed on packages are only estimates that are based on several assumptions, one of which is that the product has been kept at the constant, recommended temperature. This assumption is not always true since perishables are almost always exposed to temperature fluctuations over the course of the custody chain, with bacterial growth increasing at warmer temperatures. To keep tabs on the real state of perishable products' current quality, researchers have proposed various types of time–temperature indicators (TTIs), including electronic TTIs and others that rely on physicochemical reactions. However, these devices have proven to be either too expensive or lacking adequate device customization for different scenarios.

Seeking a new paradigm, Zhang *et al.* (DOI: 10.1021/nn401266u) developed TTIs based on plasmonic metal nanocrystals. The basis for these new TTIs is a reaction that causes epitaxial overgrowth of a Ag shell on Au nanorods, leading to visible color changes and changes in the plasmon resonances. The temporal duration of this reaction can be tuned using several different parameters, including temperature. Additionally, by introducing various weak acids, the apparent activation energy can also be tuned, which allows this device to account for fluctuations in temperature. The authors show through various proof-of-principle demonstrations that this novel TTI provides an accurate estimate of *E. coli* growth in media at three or more arbitrary temperatures over time. They suggest that this inexpensive, environmentally friendly technology could eventually revolutionize the food, beverage, pharmaceutical, and cosmetic industries.



Revolutionary Mechanism behind the Phi29 Nanomotor

■ Nanomotors are ubiquitous throughout biological systems. One particular type of nanomotor, the AAA+ superfamily of proteins, is responsible for a wide range of functions, including DNA translocation, and has been studied for nanotechnological applications. One well-studied AAA+ nanomotor, found in the Phi29 bacteriophage, has three coaxial rings, including a dodecamer channel, a hexameric ATPase ring, and a hexameric pRNA ring. Since the late 1970s, the most popular model for DNA translocation in this nanomotor proposed that DNA translocation was accomplished through rotation of at least one of the coaxial rings or of the double-stranded DNA itself. However, more recent data suggests that none of these components rotate during DNA translocation, leaving the real mechanism behind this phenomenon a mystery.



To elucidate DNA translocation in this Phi29 nanomotor, Zhao *et al.* (DOI: 10.1021/nn4002775) performed a variety of assays and reached the surprising conclusion that the mechanism appears to involve revolution rather than rotation. In essence, on binding of ATP, the channel's ATPase changes its conformation, which revolves DNA within the nanopore in one direction. The tilt of the channel subunits leads to an antiparallel arrangement of DNA's two helices, which advances DNA further within the channel. Internal channel loops keep DNA advancing unidirectionally without reversing. Only one DNA strand interacts with the channel wall at a time. Additionally, four electropositive layers in the channel interact with DNA's electronegative backbone, leading to four relaying transitional pauses during translocation. The authors suggest that a better understanding of this channel's operating mechanism could aid in integrating it into nanotechnological devices.

A New Look at Neuronal Voltage Sensing

■ Neurons do not operate in isolation. Consequently, researchers have long been interested in trying to elucidate the interactions and network dynamics of large groups of neurons. Toward this goal, biophysicists have developed various optical sensors of neuronal membrane voltage to detect action potentials visually in individual cells to understand complex interactions better. These sensors include genetically encoded fluorescent Ca^{2+} indicators. But, although Ca^{2+} dynamics provide a useful correlation with neuronal spiking, the slow kinetics and saturation of the resulting fluorescent signals limit the utility of this method. Similarly, numerous voltage-sensor indicators have been developed, but these have propensities toward photobleaching, phototoxicity, and nonspecific background labeling.

Seeking a new way to peer at the electrical activity of large populations of neurons concurrently, Marshall and Schnitzer (DOI: 10.1021/nn401410k) looked to quantum dots and other semiconductor nanocrystals. These materials have well-studied voltage-dependent optical properties, including changes in fluorescence intensity and shifts in emission wavelength. The researchers investigated how these qualities might be useful for implementing quantum dots as optical reporters for neuronal activity. Their calculations reveal that neuronal spiking can induce a 5% increase in fluorescence, as well as a ~1-nm shift in emission wavelength, in single-material quantum dots. By using quantum dots composed of two different materials, the change in fluorescence intensity was increased to 30%. The authors suggest that quantum dots within neuronal membranes could hold the key to reporting voltage dynamics in multiple neurons and over a range of optical and neurophysiological conditions.