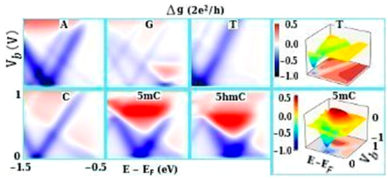
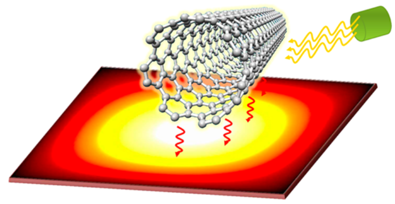
DNA Polymerase Pumps It Up

Many artificial nano/micromotors and micropumps have been designed to mimic those found in nature. The inspiration for these designs are precise and efficient motor proteins including kinesins, myosins, and dyneins. Recently, researchers have been expanding this repertoire to include enzyme-based artificial motors, which take advantage of the mechanisms many organisms use for driving biased motion in response to stimuli including chemicals or light. The diversity of these enzymatic systems could spur a wide array of nanotechnological and medical advances, such as novel dynamic self-assembly of superstructures, drug delivery, and lab-on-a-chip devices.

Seeking new candidates for enzyme-based artificial motors, Sengupta *et al.* (DOI: 10.1021/nn405963x) investigated T4 DNA polymerase, a well-characterized biomotor responsible for sequentially incorporating nucleotides to synthesize DNA. Using the ultrasensitive technique known as fluorescence correlation spectroscopy, the researchers found that the diffusive movement of DNA polymerase complexed to a DNA template increased during nucleotide incorporation into the template. The complex's diffusion coefficient was also strongly linked with its inorganic cofactor, Mg^{2+} ions. In gradients of either 2′-adenosine triphosphate (dATP) or Mg^{2+} ions, DNA-polymerase complexes moved collectively toward higher concentrations, suggesting the potential for using these complexes as fluid pumps. To test this possibility, the researchers immobilized DNA-polymerase complexes onto patterned gold surfaces, showing that in buffer solutions with dATP and Mg^{2+} ions, the complexes moved sulfate-functionalized polystyrene beads toward the gold surface. The authors suggest that these and similar complexes could eventually serve as engines for smart micro- and nanoscale devices that turn on or off in the presence or absence of analytes.



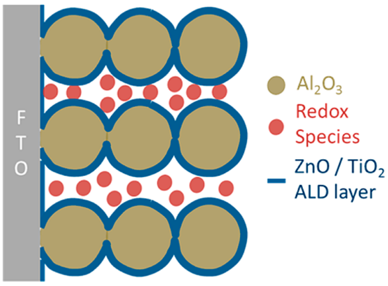
Spaser: The Final Frontier?



Because it is possible to use surface plasmons to carry information at the nanoscale, nanoplasmonics offers tremendous potential for fabricating ultrafast nanocircuits with miniaturization beyond the diffraction limit of electromagnetic waves. To power these circuits, it is necessary to incorporate a device similar to a transistor in electronics or a laser in optics. To generate surface plasmons, researchers have explored the idea of using a device known as a spaser, an acronym for "surface plasmon amplification by stimulated emission of radiation." A spaser consists of a plasmonic resonator coupled to a gain medium to replenish energy losses. To optimize performance, many spaser designs have been proposed and analyzed. However, all of these designs were based on noble metal plasmonic nanocavities coupled to semiconductor quantum-dot/quantum-well gain media.

Searching for a fresh take on spasers, Rupasinghe *et al.* (DOI: 10.1021/nn406015d) theoretically explored an all-carbon spaser with a graphene nanoflake (GNF) plasmonic resonator coupled to a carbon nanotube (CNT) gain element. Their examination suggests that excitons of the carbon nanotube generated by optical pumping recombine and nonradiatively transfer their energy to the GNF plasmons. The system is highly tunable, with GNF width, the CNT length, and GNF doping affecting this device's performance. The authors suggest that beyond tunability, this spaser offers other advantages due to its all-carbon design, such as mechanical strength and thermal stability. Consequently, devices employing nanocircuits with such a spaser would also inherit these favorable properties. They add that spasers with this design could have a wealth of applications, including ultrafast processors, flexible electronics, and biomedical sensing.

ZnO and TiO_2 Go Head to Head



Dye sensitization has provided a significant boost to molecular photovoltaics, enabling independent tuning of light-absorbing chromophores and charge-transporting layers. This division, unlike conventional *p-n* junction devices, has allowed the development of panchromatic sensitizers that absorb the entire visible solar spectrum, providing photovoltaic power conversion efficiencies that exceed 12%. The electron transport layer is typically a mesoporous oxide. TiO_2 is currently the material of choice for dye-sensitized solar cells, but the electron transport rate is low because of low electron mobility. Consequently, ZnO has been considered as a potential electron transport layer candidate due to its significantly higher mobility, but its power conversion efficiency is still lower than that of TiO_2. Because of a variety of morphological differences between films of these two materials, researchers have yet to make a one-to-one comparison between TiO_2 and ZnO dye-sensitized solar cells.

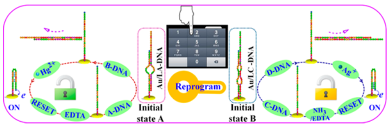
Finally bringing this issue to the fore, Chandiran *et al.* (DOI: 10.1021/nn405535j) were able to compare these two materials' photovoltaic performance and electron transfer dynamics accurately by depositing different thicknesses of these oxides by atomic layer deposition on an arbitrary mesoporous insulating template and using them as photoanodes in dye-sensitized solar cells. The researchers' results suggest that at an optimal thickness of 5 nm, ZnO shows photovoltaic performances similar to TiO_2, but the reasons for comparable performances differ. ZnO's higher photogenerated electron transport rate made up for TiO_2's low recombination rate, higher dye loading, and fast electron injection. The authors suggest that each material might be used in situations where its best attributes might lend an advantage.

10.1021/nn501457q

What's the Password? DNA

Computing, information processing, and data storage at the molecular level continue to attract increasing attention. Thus, finding a way to prevent data and information in these systems from unauthorized invasion is a growing priority. Consequently, researchers have developed a variety of molecular security systems, including molecular keypad locks whose output of opening access to data depends strongly on the exact combination and sequence of inputs, akin to a computer password. Because this password might be cracked or accidentally disclosed, it is advantageous to have a keypad lock that could by reprogrammed to accept a new password. Additionally, the ability to allow multiple users to access data in a hierarchical fashion, giving an administrator priority over guest users, would also be useful.

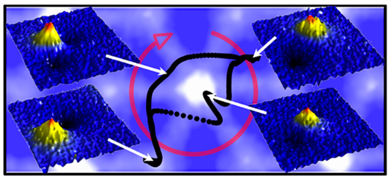
In a recent advance, Li *et al.* (DOI: 10.1021/nn406523y) developed a novel molecular keypad lock with these unique and valuable characteristics based on DNA. The researchers tethered one strand of ferrocene functionalized DNA to a gold electrode and attached a partially complementary strand to set the lock in its initial state. Then, using a fully complementary strand or mercury ions as inputs, they designed a password in which the ferrocene groups of the tethered strand moved closer to the electrode or remained far away based on interaction with the attached partially complementary strand, corresponding to the lock opening or remaining closed. Using different inputs, the researchers were able to reprogram the system to accept a new password and to allow multiple, hierarchical users. The authors suggest that designing a molecular keypad lock with even more functionality will be possible in the future.



Peering into the Vortex for NbSe$_2$

Researchers are becoming increasingly interested in the dynamics of nanoscale objects, a field that has numerous technological implications. The ability to control these motions, through electromagnetic fields, current, temperature, or other methods, could advance the construction of useful nanodevices. To understand and to exploit nanoscale dynamics fully, it is crucial to visualize these systems directly. Static systems with objects down to the atomic scale, including the superconducting state, have been visualized using scanning tunneling microscopy (STM). Yet, this technique suffers from large capture times, making it unsuitable to study dynamic events.

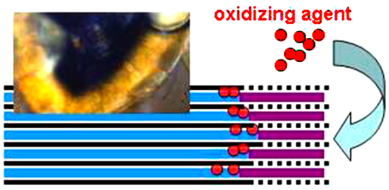
Seeking a new way to visualize nanoscale dynamic phenomena, Timmermans *et al.* (DOI: 10.1021/nn4065007) studied the vortex matter in NbSe$_2$ by driving the superconducting vortices using an AC magnetic field in STM and examining the induced periodic tunnel current modulations. Using a lock-in amplifier, the researchers observed the direction and amplitude of oscillating vortices with respect to NbSe$_2$'s Abrikosov lattice. They also constructed real-time videos to visualize the trajectory of the moving vortices dynamically. With clarification from the second technique, the researchers showed that collectively, the vortex trajectory is a nano-orbit, starting along the channels of depleted superconductivity and avoiding the main axis of the Abrikosov lattice, consistent with the single vortex regime. The authors suggest that this technique can be extended to other scanning probe microscopy techniques to examine other periodic phenomenon dynamically, either spontaneously or where the periodicity can be induced.



Go Time for Examining Graphene Oxide Formation

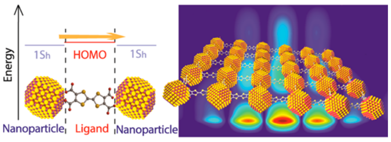
Interest in graphene oxide (GO) surged in 2004 related work on by graphene. This material, derived from graphene by introducing covalent C–O bonds, has the ability to remain exfoliated in water, cast as films, and reduced back to graphene. These unusual characteristics give it the potential for use in numerous applications including electronics, conductive films, electrode materials, and composites. Researchers have made significant forward progress in understanding GO chemistry and structure, yet little is known about its mechanism of formation. Most reported studies thus far are theoretical and have failed to take into account the dynamics introduced by precursor graphite's closely aligned and stacked layers.

To gain a better understanding of GO formation, Dimiev and Tour (DOI: 10.1021/nn500606a) prepared GO using a modified Hummers' method, which involved adding 5 weight equivalents (wt equiv) of KMnO$_4$ to 1 wt equiv of graphite. They stopped the reaction after adding 1, 2, 3, and 4 wt equiv of KMnO$_4$, identifying three distinct intermediate products. The first step converted graphite into a stage-1 graphite intercalation compound with a deep blue color within minutes. The second step converted this compound into oxidized graphite, which the researchers dubbed pristine graphite oxide (PGO), over hours or days, leading to light brown or yellow oxidized areas to appear at the graphite flake edges. In the third step, PGO converted to conventional GO in water. The authors suggest that these intermediates, which can be isolated, characterized, and stored, offer a critical view of the mechanism behind GO formation.



Tipping a Cap to $TTFTA^{4-}$

Combining organic and inorganic nanostructures can produce materials with the best of both worlds: organic semiconductors' chemical versatility and inorganic nanomaterials' chemical stability and size-tunable band gaps. These hybrid nanostructures have often been prepared by mixing the organic and inorganic components in a solvent, then solution-processing the mixture into a thin film. However, this convenient protocol can lead to phase separation between the organic and inorganic moieties, leading to inefficient coupling between the organic and inorganic constituents and ill-defined interfaces. To avoid this shortcoming, one strategy is to functionalize the organic component with a coordinating group that can bind directly to the inorganic nanostructure. Such inorganic–organic core–shell structures have often been fabricated with dendronized polymers, but the large size of these molecules can adversely affect in-film charge carrier transport.

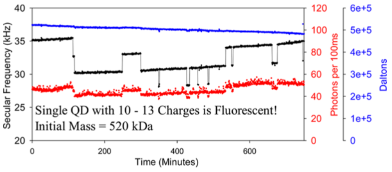


Seeking a better solution, Scheele *et al.* (DOI: 10.1021/nn406127s) turned to tetrathiafulvalenetetracarboxylate ($TTFTA^{4-}$), a derivative of the small and simple organic semiconductor tetrathiafulvalene. Starting with films of PbS nanocrystals capped with $Pb[Oleate]_2$, the researchers performed a ligand exchange with $TTFTA^{4-}$ to create films of PbS-TTFTA core–shell semiconductor nanoparticles. Microscopy studies and grazing incidence small-angle X-ray scattering show that in-film order is largely preserved in the films after ligand exchange. Incorporating the films in field-effect transistors, the researchers found unusually large mobility compared to nonconjugated ligands comparable in length. Further investigation suggests that these results are due to a near-resonant alignment of the PbS $1S_h$ state and the organic HOMO. The authors suggest that this method holds promise for designing ordered, coupled nanoparticle thin films.

Trapping Quantum Dots, Releasing New Understanding

Nanoparticle mass spectrometry (NPMS) and optomechanical levitation provide a unique way of studying the physical and optical properties of levitated nanostructures as they undergo various manipulations. This method involves trapping a single, charged nanoparticle in a quadrupole ion trap, then using light scattering or laser-induced fluorescence to detect and to track the particle's motion. By allowing for repeated and nondestructive measurements of the mass (M) and charge (Q) of single trapped nanoparticles over the course of hours or days, these techniques make it possible to correlate these measurements and others as the particles are heated, exposed to reactants, and given other treatments. This technique could add insight into the behavior of quantum dots (QDs) when they are charged and detached from a surface.

In a new study, Bell *et al.* (DOI: 10.1021/nn405920k) use NPMS to explore the optical properties of single core–shell CdSe/ZnS nanocrystals isolated in the gas phase in a quadrupole ion trap. Results showed that the emission spectra of the trapped QDs were significantly red-shifted compared to emission from the same particles in solution. After heating the particles to the point of sublimation, the researchers found that the QDs remained emissive up to 85% mass loss, with the emission proportional to the QDs' surface area. They eventually reached a point where their fluorescence quantum yield dropped suddenly and they began to blink. The researchers note that NPMS is versatile and will allow exploration of how QD optical properties correlate with mass and charge as a function of various manipulations.



New Dimension of Insight on Three-Dimensional Protective Monolayers

To prevent Au nanoparticles from aggregating and to display functional groups for potential applications, they are sometimes capped with monolayers of another material. The most common type of these monolayer protected clusters (MPCs) is $Au_{25}(SR)_{18}$. Although these MPCs are usually represented as three-dimensional (3D) equivalents of two-dimensional (2D) self-assembled monolayers (SAMs) on extended Au surfaces, it is unclear how similar these two structures really are. While 2D SAM molecular adsorbates interact primarily through interchain van der Waals forces, leading to the formation of regular domains of parallel molecules, researchers do not yet know whether these interactions are important or even present in MPCs. Some evidence suggests that 3D MPCs are indeed distinct from 2D SAMs. For example, while 2D SAMs are compact enough to prevent penetration of molecular probes, electrochemistry experiments suggest that MPC monolayers allow some solvent and electrolyte penetration.

To characterize MPCs in solution, Antonello *et al.* (DOI: 10.1021/nn406504k) prepared a large series of monodisperse $Au_{25}(SC_nH_{2n+1})_{18}$ clusters, with n = 2, 4, 6, 8, 10, 12, 14, 16, 18. Electron transfer experiments suggest that up to n = 12, the MPCs form a fluid monolayer structure, but beyond this critical length, the MPCs self-organize into bundles. These results were consistent with ^1H nuclear magnetic resonance spectroscopy, infrared absorption spectroscopy, and molecular dynamics simulations. Further experiments show that unlike 2D SAMs, the Au_{25} core is able to communicate efficiently with the outer environment even for MPCs with long alkyl chains. The authors suggest that these results shed light on the significant distinctions between 2D SAMs and 3D MPCs.