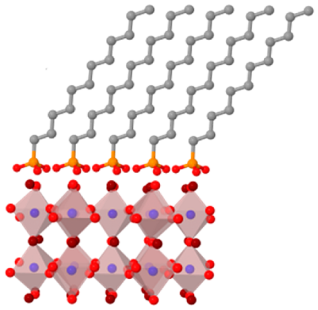
Half-Metallic Manganite Goes Undercover with Self-Assembled Monolayers

Spintronics, a technology that exploits electrons' inherent spin and the associated magnetic moment, has relied heavily on (La,Sr)MnO_3 manganite (LSMO) as the standard ferromagnetic electrode in organic devices because of its highly polarized spin and stability in air. Thus far, researchers have primarily looked to organic semiconductors and polymers to propagate spin in these devices. Self-assembled monolayers (SAMs), which have been used primarily to tune the chemical and physical properties of metal–organic interfaces, could potentially be a promising replacement for these materials in molecular spintronic devices. However, to fill this role, researchers first need to develop a protocol for grafting SAMs onto LSMO.

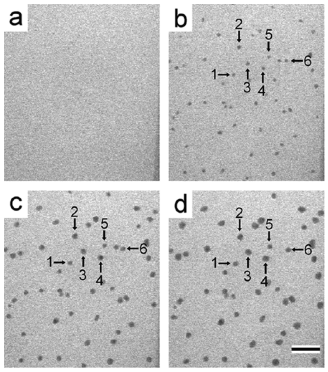
In a new study, Tatay *et al.* (DOI: 10.1021/nn302458z) fill this gap by grafting two different phosphonic acid SAMs onto LSMO. To find the best material to functionalize the half-metallic oxide surface, the researchers tested different combinations of common organic solvents and dodecyl carboxylic acids, octadecyl/dodecyl phosphonic acids, octadecyl silanes, octadecyl aminos, and octadecyl thiols. Tests showed that only the alkyl phosphonic acids produced noticeable differences in water advancing contact angles, suggesting that these acids were effectively binding to the LSMO surface. A variety of characterization methods showed that grafted dodecyl and octadecyl phosphonic acids formed ordered SAMs on LSMO, with the phosphonic group bound to the oxide surface and alkyl chains tilted away at angles of 43 and 27°, respectively. Incorporating these materials into nanosized electrodes, the researchers found that they act as tunnel barriers. The authors suggest that these findings open the door for incorporating SAM-covered LSMO into spintronic devices such as spin organic light-emitting diodes.



Peering at Nanoparticle Nucleation and Growth

Nanocrystals' properties can be customized by controlling their morphology and size, an effect quite unlike most macroscopic materials. Although these properties can be effectively tuned using conventional colloidal synthesis, researchers needed an armamentarium of characterization techniques to determine key properties such as nucleation rate, induction time, growth rate, and resulting morphology. Recent findings have shown that scanning transmission electron microscopy (STEM) can be used for the dual purpose of both growing nanocrystals by electron beam reduction as well as observing growth at the single nanocrystal level. However, these observations turned up morphologies consistent with two different growth mechanisms for nanocrystals grown using similar electron beam parameters.

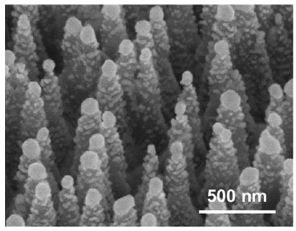
To understand how these different morphologies arise, Woehl *et al.* (DOI: 10.1021/nn303371y) grew silver nanocrystals in an *in situ* fluid stage with STEM, using the electron beam for both observation and reduction to stimulate growth. Results showed that changing the current density, pixel dwell time, and magnification changed the time it took to induce nanocrystal nucleation but had no effect on the electron dose needed to induce nucleation. After this threshold dose was met, the researchers found that the electron beam itself largely dictates both how the nanocrystals grow and their resulting morphology. Essentially, their findings show that, at beam currents near this threshold, the nanocrystals grew by a reaction-limited mechanism, leading to faceted structures. In contrast, beam currents about seven times larger than the threshold resulted in a hindered, diffusion-limited mechanism, leading to spherical structures. The authors suggest that the electron beam plays a role much like that of the reducting agent in conventional synthesis.



Probing Kinase Phosphorylation with Electricity

Biomolecules have a dizzying array of responses to external stimuli, such as mechanical, thermal, optical, and electrical inputs, with the resulting outputs useful for a variety of applications. Some stimuli can induce compositional or structural changes, and finding ways to measure these effects could turn biomolecules into components of useful sensors for clinical or other uses. For example, kinases, which activate proteins by transferring a phosphate group, have differing conformations if they are phosphorylated. Because kinases can play roles in cancer, diabetes, and other diseases if their activity is dysfunctional, probing whether kinases are phosphorylated could prove to be a useful clinical tool.

In a new study, Chen *et al.* (DOI: 10.1021/nn3027408) bring this concept closer to fruition by applying an electric field across peptide



probes, exaggerating differences in conformation between phosphorylated and nonphosphorylated varieties that are then detectable through surface-enhanced Raman spectroscopy (SERS). The researchers attached a synthetic peptide sequence to a gold surface suitable for SERS. When this peptide was phosphorylated, it induced a net negative charge, leading it to interact with the positively charged metal surface. When the researchers introduced a positive or negative electric field, the phosphorylated peptides caused a change in the SERS signal, while the nonphosphorylated peptides showed no response. Molecular dynamics simulations matched the SERS data and suggested a mechanism, showing that changes in the electric field caused the phosphorylated peptide to coil or to stretch, depending on whether the applied field was positive or negative. The authors suggest that this electro-optical detection and manipulation method could prove useful for other biomolecules, as well.

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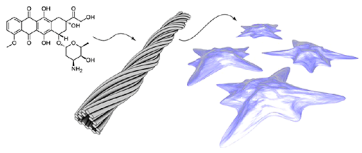
Cancer Therapeutics Delivery, with a Twist

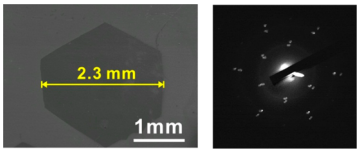
Because of its intrinsic Watson–Crick base-pairing and easy functionalization with drugs and ligands, DNA can be manipulated into customized formations that could be useful for a variety of applications, including targeted drug delivery. Although this technique has been used to produce nanostructures to deliver different cargoes to cells, such as immunostimulatory oligonucleotides, researchers have not yet explored so-called DNA origami to deliver many other drug types, such as anthracyclines. Anthracyclines work by intercalating DNA and thus could be a natural fit for delivery by DNA origami nanostructures.

To determine the feasibility of this approach, Zhao *et al.* (DOI: 10.1021/nn3022662) fabricated two different types of DNA origami nanostructures, testing whether alterations in the amount of twist could change drug loading and release properties for doxorubicin, a commonly used cancer anthracycline. The researchers designed two 18-helix bundle nanotubes, one a straight nanotube (S-Nano) with 10.5 bases per helical turn, and the second a twisted version (T-Nano) that had 12 bases per helical turn due to an insertion per every seventh base pair. After loading both nanostructures with doxorubicin, tests showed significant differences in release kinetics between the two designs, with T-Nano retaining significantly more of the drug over time and releasing it more slowly than S-Nano. Additionally, T-Nano encapsulated 33% more doxorubicin than S-Nano. Using three different breast cancer cell lines as models, the researchers show that the T-Nano system delivered doxorubicin more efficiently to the cells, leading to higher cancer cell death. The authors suggest that this design could offer a promising new targeted drug-delivery system.



Graphene Goes Large

Single-crystal graphene's superior electrical and physical properties make it a promising material for many potential applications. However, fabrication methods thus far have not been able to produce high-quality graphene in sizes large enough for these purposes. Although chemical vapor deposition (CVD) methods have realized larger scale and uniform polycrystalline graphene, the resulting products' electrical properties are limited by the inherent domain boundaries. To avoid this problem, some recent studies have focused on fabricating single-crystal graphene using CVD on transition metals, including Cu, with resulting domains as large as a millimeter. However, even larger sizes are necessary to bring commercial applications to fruition.

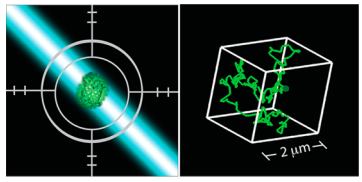


Pushing the boundaries of size, Yan *et al.* (DOI: 10.1021/nn303352k) developed a novel method to produce graphene domains as large as 4.5 mm^2 using Cu foils as a substrate. The researchers first cleaned the Cu surfaces using an electrochemical polishing method. Then, using CVD with controlled chamber pressure, they annealed the Cu surface under high heat and pressure, then lowered the pressure before adding graphene precursor CH_4. Microscopy revealed the resulting graphene domains' large sizes, with the largest being more than 20 times greater than the best previously reported results on Cu, which the researchers credited to a limited number of nucleation sites. Various characterization methods indicated that the graphene produced had a single-crystalline, monolayer structure with few defects. By incorporating this product into Hall bar field effect transistors, they found that the synthesized graphene had high carrier mobilities similar to exfoliated graphene. The authors suggest that their methods could be further optimized to produce even larger single-crystal graphene on Cu.

Keeping a Watchful Eye on Single Molecules

Single-particle tracking has proven to be a useful tool for better understanding a variety of phenomena, including bacterial chemotaxis, membrane dynamics, and motor protein kinetics. In the past few years, researchers have expanded this concept to include single-molecule tracking (SMT), which involves following a single quantum emitter such as an organic dye, fluorescent protein, or quantum dot through time and space, often attached to a biomolecule of interest. Most SMT systems to date have used a wide-field imaging microscope with an array-based camera, such as a charge-coupled device, to track molecules inside a single two-dimensional detection plane. However, this method is not useful for following the majority of cellular functions, such as intracellular signaling and protein trafficking, which occur in three dimensions and across extended distances.

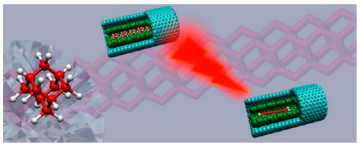
Seeking an imaging protocol that would be useful for these biological functions, Han *et al.* (DOI: 10.1021/nn302912j) developed a method for tracking single organic dye molecules and fluorescent proteins in three dimensions over distances as large as several micrometers and at rates up to 1 $\mu m^2/s$. The novel method involved using a stage scanning confocal microscope with a spatial filter and active feedback that continually adjusts the stage to keep the tracked molecule close to the center of the confocal excitation probe volume. The researchers show the feasibility of this technique for two different organic dyes as well as the fluorescent protein Azami Green, with time-resolved spectroscopy demonstrating that the tracked trajectories were single molecules. Furthermore, they showed that their technique could determine protein oligomerization states using Azami Green monomers, dimers, and tetramers as a model. The authors suggest that their new technique could shed light on a variety of biological phenomena.



Within the Confines of Carbon Nanotubes

Diamondoids, sp^3-hybridized, carbon-based molecules with diamond-shaped morphologies terminated by hydrogen, have a wide array of interesting and useful properties. These molecules have been exploited for pharmaceuticals and high-temperature polymers, and their unique electrical and thermal properties suggest a variety of other potential applications. Diamondoids fit into carbon nanotubes, and consequently, this constrained space provides a way to form linear arrays of these molecules through self-assembly. Carbon nanotubes' narrow cavities also could provide a constraint to direct reactions that produce other interesting nanostructures.

To that end, Zhang *et al.* (DOI: 10.1021/nn303461q) used theoretical and experimental studies to examine the smallest diamandoid, adamantane, inside the restricting spaces of double-wall carbon nanotubes

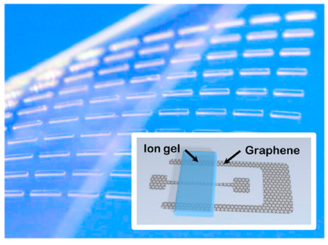


(DWCNTs). Using a vapor-phase reaction, the researchers assembled linear arrays of adamantane inside DWCNTs. They found that the ability to form these arrays was highly dependent on the diameter of the nanotubes. Various characterization methods showed that no encapsulation took place in DWCNTs with diameters below 0.8 nm, while single linear arrays were present in nanotubes with diameters of about 1.0 nm, and multiple linear arrays were present when nanotube diameters exceeded 1.3 nm. Depending on the surrounding atmosphere and annealing conditions, the researchers found that these encapsulated molecules could react inside the DWCNTs, forming carbon chains detected by Raman spectroscopy after vacuum annealing at 500 °C. However, when annealed at higher temperatures in a pure hydrogen atmosphere, the adamantane remained unreacted, suggesting that hydrogen maintained the sp^3-hybridized carbon structures. The authors suggest that these new findings provide insight into the behavior of diamandoids encapsulated into the confines of carbon nanotubes.

Transparent Flexible Graphene Transistors: A Two-Ingredient Recipe

Graphene's optical transparency, mechanical flexibility, and high carrier mobility make it a natural choice for use in transparent, flexible electronics. Consequently, researchers have developed an array of printing methods to assemble graphene thin film transistors (TFTs). However, these methods all involve numerous steps. Simplifying graphene TFT synthesis through fewer printing steps would represent a significant step forward in assembling these devices.

Toward that end, Kim *et al.* (DOI: 10.1021/nn3020486) created transparent flexible graphene transistors and inverters using only two materials: graphene and an ion gel gate dielectric. Starting with monolayer graphene, the researchers used photolithography and oxygen plasma etching to form multiple strips and split arms. They transfer-printed these graphene patterns onto a substrate for the TFT, with the main strip functioning as a semiconducting channel and the split arms, patterned to be coplanar with the main strip, serving as the gate electrode. Finally, the researchers used an aerosol jet printing technique to add the ion gel gate dielectric across the split arms and a portion of the main graphene strip. Tests showed that these devices exhibit good optical transparency, have high hole and electron mobilities, and were produced with more than a 95% yield. Flexing these TFTs, even thousands of times, did little to change their properties. These devices were also stable in air after more than a month of storage. Additionally, the researchers demonstrated that these TFTs could be assembled into inverters by connecting two coplanar gate transistors on a plastic substrate. The authors suggest that this simple design could hold promise for advancing graphene TFTs in thin, flexible, transparent electronics.



DNA Nanoconstructs: From Watson–Crick to Click

In recent years, researchers have capitalized on DNA's natural Watson–Crick base-pairing to create nanostructures with enormous complexity. One popular way to shape this genetic material into desired configurations is DNA origami, which involves folding long strands of bacteriophage DNA into predetermined shapes that are then held in place with shorter oligonucleotide staples. Although this technique has been employed to form numerous interesting structures, such as DNA smilies and three-dimensional nanoboxes, DNA origami and other methods that rely purely on hybridization suffer inherent thermodynamic instability. One way to avoid this problem is to rely on chemically synthesized DNA that cross-links through reactions other than hybridization.

In a new study, Gerrard *et al.* (DOI: 10.1021/nn3035759) demonstrate a new way to form DNA nanoassemblies that involves modular nanostructures of chemically synthesized DNA joined together through a click chemistry reaction. The researchers linked together short snippets of DNA modified at their ends with a 3-cyanovinylcarbazole (^{CNV}K) moiety incorporated during synthesis. This ^{CNV}K moiety allowed the strand ends to be cross-linked through a photochemical reaction, creating DNA hexagons. Tests showed that these photochemically cross-linked DNA nanoconstructs could be purified through polyacrylamide gel electrophoresis and were stable with respect to heat and denaturing agents, allowing them to be characterized by mass spectrometry. Using an orthogonal click chemistry reaction that had not previously been used on DNA nanostructures, the researchers were able to join separate rings into dimeric, trimeric, and oligomeric configurations. The authors suggest that this new assembly method could be used to construct DNA nanomachines and functional nanoarchitectures.