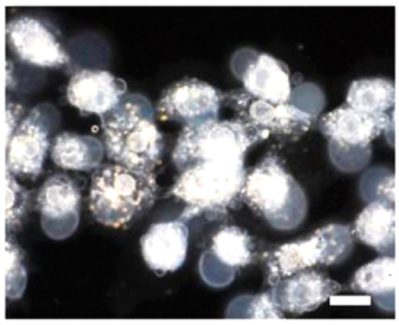
New Insight as Cells Go into That Dark Night

Researchers have long sought better understanding of apoptosis, the programmed cell death that plays roles in a number of important bioprocesses and cellular functions, including normal tissue development and advancing many acquired diseases. This complicated process is regulated by many different proteins and molecular signals that work in concert to initiate downstream cellular and molecular events. Although this intricate phenomenon has yet to be completely elucidated, apoptosis' later stages both on the cellular and molecular levels have been well characterized, including membrane blebbing, nuclear fragmentation, and nuclear protein denaturation. Finding a way to follow these events in real time could give researchers more insight on the mechanisms and pathways involved in apoptosis.

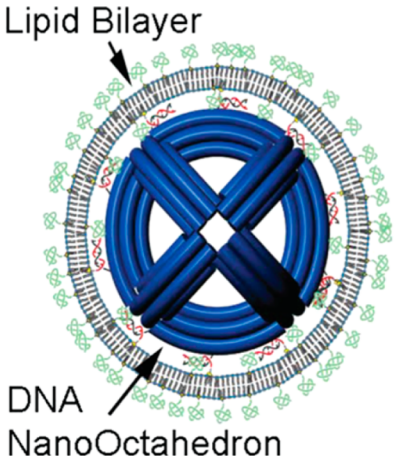
Toward this end, Kang *et al.* (DOI: 10.1021/nn500840x) developed a novel method to observe morphological and molecular events of apoptosis while they are occurring. The researchers first used targeted gold nanospheres that amplify the Raman signals of molecules in the cell nucleus to create a reference profile for a series of changes that might relate to apoptosis. Then, after inducing apoptosis in human oral squamous cell carcinoma cells by exposing them to H_2O_2, the researchers watched the cells with Rayleigh imaging and Raman spectroscopy. Matching the reference profiles to Raman bands they collected in the cell experiments, the study authors created a temporal profile of apoptotic events, showing protein denaturation through disulfide bond breakage and DNA fragmentation, followed by protein unraveling, and finally protein degradation. The authors note that this method could be used to compare apoptosis induced through other methods.



A DNA Nanostructure in Virus Clothing

The ability to arrange DNA into molecular-scale devices with exacting control over geometry and site-specific functionalization promises significant advances in biomedical technology. Researchers have recently developed a variety of new DNA-based nanoscale devices that could accomplish several different biomedical aims, including a nanorobot, programmable immunoadjuvants, a synthetic membrane channel, and a molecular cascade that can autonomously process multiple inputs to determine cell phenotype. Despite this potential, translating DNA nanotechnology into biomedical applications will require scientists to devise ways to protect these devices from nuclease degradation and to prevent them from activating an inflammatory immune response.

Inspired by nature, Perrault and Shih (DOI: 10.1021/nn5011914) used enveloped viruses as a model system to accomplish both of these goals. The researchers mimicked the geometry

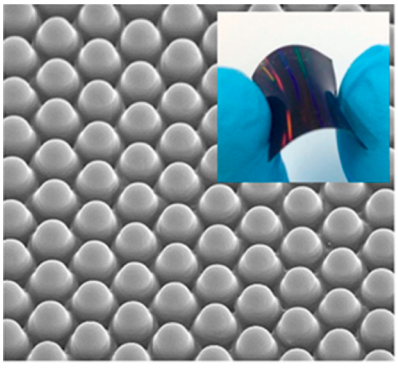


of a viral protein capsid shell by creating a wireframe DNA nanooctahedron (DNO) using bundles of DNA double helices as struts. To these, they attached DNA "handles" for functionalization. On handles that protruded inside the DNO, they attached fluorophore-conjugated oligonucleotides for optical contrast. On those that protruded outside the DNO, they attached lipid-conjugated oligonucleotides, enabling a PEGylated lipid bilayer to assemble around the structure. Tests showed that DNA nanostructures surrounded by these lipid bilayers were effectively protected from nuclear digestion, were significantly less likely to provoke an immune response, and increased pharmacokinetic bioavailability several orders of magnitude beyond similar structures that lacked surrounding lipid bilayers. The authors suggest that this design strategy could move DNA nanostructures significantly closer to biomedical applications.

More Than One Way to Electronic Skin

Human skin possesses a variety of unique capabilities, including sensitivity to pressure, shear, strain, temperature, humidity, fluid flow, and pain. These exceptional properties have made it a target for synthetic reproductions in the form of electronic skin. Researchers have proposed and tried several different ways to realize flexible and sensitive electronic skins, including systems based on piezoresistive composite elastomers. Although these materials have shown great promise toward this end, they have several drawbacks that have prevented their future development in electronic skin applications, including poor sensitivities, long response times, and signal drifts with temperature.

In a new study, Park *et al.* (DOI: 10.1021/nn500441k) developed a novel design for conventional piezoresistive composite films that offers a way around these drawbacks. The researchers created novel films by loading a liquid



mixture of carbon nanotubes, polydimethylsiloxane prepolymer, and a curing agent into silicon molds to create microdome arrays. When two of these molded microdome arrays are placed with the patterned sides facing each other and the domes are interlocking, tunneling resistance increases significantly at contact spots, leading to giant tunneling piezoresistance. Tests show that this property translates into high sensitivity to pressure and rapid response and relaxation times that are not significantly affected by variations in temperature. The novel electronic skin could detect and distinguish stimuli as varied as different letter-shaped weights, the movements of a snail, human breathing, and voice vibrations. The authors suggest that this design gives a boost to the field of electronic skin and has potential for use in wearable health-monitoring systems.

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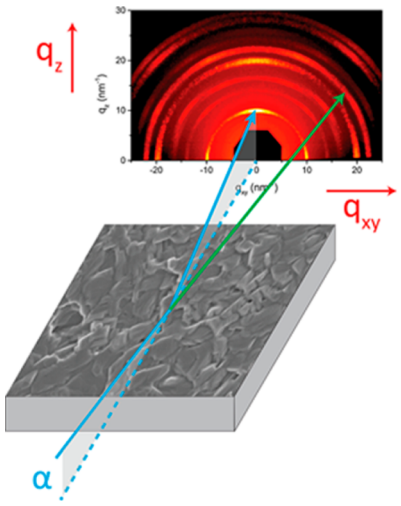
Shining a Light on Solution-Processed Hybrid Perovskites

Thus far, thin film hybrid solar cells made with solution-processable materials, including semiconductor nanocrystals and dye-sensitized solar cells, have achieved power conversion efficiencies (PCEs) of 7−12%. New research suggests that highly efficient solid-state hybrid perovskite solar cells can push PCEs higher than 15%. The methylammonium lead trihalide ($CH_3NH_3PbX_3$; X = I, Br, or Cl) semiconducting perovskite offers particular promise for thin film voltaics. Incorporating this material into a block copolymer structure could further improve this material's charge transport and light management. However, to achieve optimum structural control, researchers must gain better understanding of the structural evolution of these thermally annealed materials.

In a new study, Tan *et al.* (DOI: 10.1021/nn500526t) used *in situ* grazing incidence wide-angle X-ray scattering (GIWAXS) and scanning electron microscopy to investigate the structural evolution of methylammonium

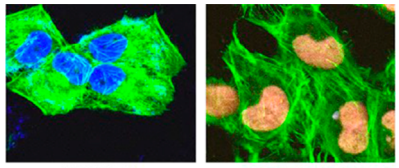


lead triiodide/chloride ($CH_3NH_3PbI_{3-x}Cl_x$) in mesoporous block-copolymer-derived alumina superstructures. Early in the annealing process, the GIWAXS profile revealed scattering peaks that were not characteristic for CH_3NH_3I, $PbCl_2$, PbI_2, or the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite structure, suggesting the formation of a crystalline precursor structure not previously described. Later GIWAXS data suggested the formation of a three-dimensional perovskite structure, and then a mixture of compounds resulting from degradation. Experimenting with annealing parameters that optimize crystalline precursor coverage and the subsequent phase transformation, factors found to be pivotal to the final film coverage, the researchers developed a block copolymer-directed perovskite solar cell with enhanced performance. The authors suggest that further design tweaks could improve PCEs for solar cells with these films even more.

Giving Cancer the One-Two-Three Punch

The vast majority of chemotherapeutic drug failures are due to tumor cells developing multidrug resistance. This effect, attributable to low tumor specificity, inadequate drug penetration to the tumor site, and hasty clearance from circulation, leads to a cascade of stronger treatments with increasingly harsher side effects. Doxyrubicin, which kills cancer cells by intercalating with DNA, is one popular cancer drug that often spurs resistance. Finding ways to increase uptake of this agent could increase its effectiveness in greater numbers of patients. Recent studies suggest that combining chemotherapy with near-infrared hyperthermia can help enhance drug uptake. Another strategy that has shown promise in the lab is targeting CD44, a cell-surface glycoprotein that is overexpressed in many solid tumors and drug-resistant cancer cells. However, thus far, no therapy has combined these various factors.

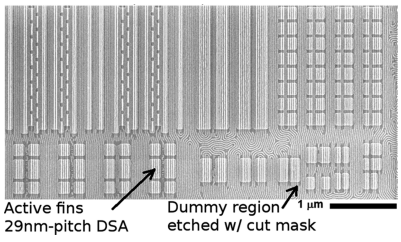
Seeking a new way around multidrug resistance, Bhirde *et al.* (DOI: 10.1021/nn501223q) developed a strategy that delivers doxyrubicin in functionalized semiconducting single-walled carbon nanotubes (sSWCNTs). Using a single-step reaction, the researchers wrapped sSWCNTs with cholanic-acid-derivatized hyaluronic (CAHA) acid biopolymer, which targets CD44. They then mixed these CAHA−sSWCNTs with doxyrubicin, which loaded the drug within, with high efficiency. Tests showed that these agents were significantly better at killing multidrug resistant ovarian cancer cells compared to doxyrubicin alone or drug-loaded sSWCNTs wrapped with poly(ethylene glycol), an effect tied to this nanoformula's effects on cells' viscoelasticity. By further capitalizing on sSWCNTs' photothermal properties, the researchers found that this novel therapeutic was able to eradicate tumors completely. The authors suggest that this combination could offer a new way to combat multidrug resistance in cancer therapy.



A Fine New Way To Craft Fins

The semiconducting industry is increasingly moving away from conventional metal-oxide-semiconductor field-effect transistors (MOSFETs) toward FinFETs, field-effect transistors composed of an ensemble of discrete single crystal Si mesas, or "fins." The raised geometry of each fin allows the gate electrode to wrap around the device, enabling improved control over the fields in the channel. Rather than applying a field to just one side of the channel as in MOSFETs, FinFETs have better performance at smaller gate lengths. The spatial frequency, or pitch, of the fins can significantly affect device performance, with denser fins leading to a reduction in parasitic capacitance. Thus far, researchers have produced a fin pitch of 60 nm using a sublithographic pitch reduction technique. However, for future process nodes, scaling the fin pitch even lower will be required.

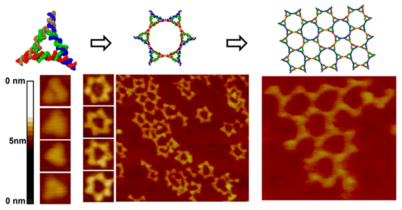
In a step toward this goal, Tsai *et al.* (DOI: 10.1021/nn501300b) developed a way to create fins with pitches as low as 29 nm using graphoepitaxy-based lamellar phase directed self-assembly (DSA) processes by taking advantage of interactions between a block copolymer and the template pattern. Using hydrogen silsesquioxane guiding patterns and a poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) block copolymer, the researchers created raised Si features in a process that involved etching away the poly(methyl methacrylate) phase followed by a tone inversion process. Testing the viability of this method, they made functional DSA-patterned FinFET devices with 29-nm-pitch fins. The authors suggest that future methods to reduce line-width and feature profile variation could improve the performance of devices made using this technique.



RNA Can Take the Heat

Researchers are increasingly looking to nanomaterials to create better products for pharmaceutical, medical, electronic, and biomedical applications. Polymers have attracted particular attention for this purpose due to their ability to improve systems' and devices' thermostability, chemical stability, strength, flexibility, and biocompatibility, among other desired qualities. However, chemical polymers also come with several disadvantages, including difficulty in controlling the size, shape, and stoichiometry of resulting products. Because RNA is a natural polymer whose self-assembly can be guided to generate structures with defined size, shape, and stoichiometry, it could be an attractive alternative to chemical polymers. However, RNA can be unstable and relatively easy to denature, partially due to the presence of a reactive hydroxyl group at the 2′ ribose.

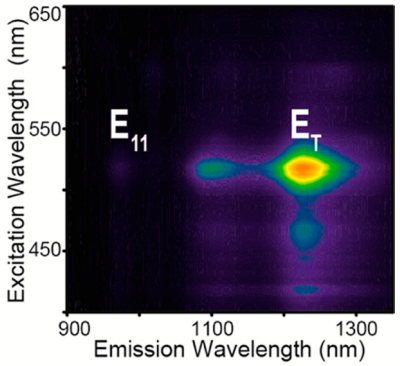
To help RNA realize its potential, Khisamutdinov *et al.* (DOI: 10.1021/nn5006254) worked with the three-way junction (3WJ) motif of packaging RNA (pRNA), a form that has been discovered to be unusually stable. The researchers created three different types of RNA triangles: one formed from normal RNA, another from a modified 2′F-U/C, and a hybrid triangle made from both types of RNA. Tests showed that the RNA triangles were able to assemble and to remain stable in the presence of 8 M urea, a strong denaturing agent, and even survived boiling. Fluorophores and therapeutic agents incorporated into these triangles did not affect the structures' overall conformations and retained their functional activity. Additionally, the researchers used the triangles to create hexagons and patterned hexagonal arrays. The authors suggest that RNA nanoparticles could hold promise for a variety of industrial and nanotechnological applications.



Carbon Nanotubes Trion New Role

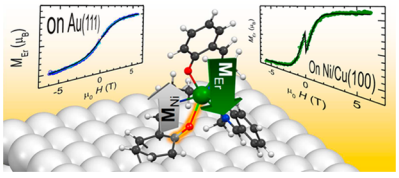
Researchers have been intrigued by trions—charged, quasiparticles composed of two electrons and one hole, or *vice versa*—ever since they were first predicted in 1958. Since then, trions have been observed in quantum wells, quantum dots, and single-walled carbon nanotubes (SWCNTs). Although trions in quantum wells and dots are unstable except at cryogenic temperatures due to their low binding energies, those in SWCNTs have a much higher binding energy, rendering them observable even at room temperature. However, when SWCNT trions have been observed thus far, they have been present only as a minority carrier.

In a new study, Brozena *et al.* (DOI: 10.1021/nn500894p) show that trions can be efficiently generated as bound quasiparticles in semiconducting SWCNTs by creating controlled sp^3 defects through chemical doping. To introduce these defects, the researchers covalently functionalized the SWCNTs using two different methods: Billups-Birch propagative sidewall alkylcarboxylation chemistry using sodium-charged liquid ammonia and oleum-based diazonium chemistry. After either type of functionalization, results showed that trion photoluminescence was observed in the emission spectrum of individually dispersed SWCNTs as a new peak that was substantially red-shifted from the E_{11} excitation. This energy shift reveals a trion binding energy as high as 262 meV, substantially larger than any previously reported trion binding energy for SWCNTs. Modified and stored SWCNTs were still able to generate trions at low excitation even months after sample preparation. The researchers suggest that these findings could be a stepping-stone to better understanding trions for basic science as well as applications in photonics, electronics, and bioimaging.



The Rules of Attraction for Single Ion Magnets

Molecular magnets have a host of intriguing features, including slow relaxation of magnetization, optical luminescence, redox activity, and spin crossover. Consequently, they have the potential to be building blocks in a variety of molecular spintronics applications. To take advantage of these useful qualities, researchers have deposited them onto substrates with monolayer or sparser coverage, allowing access to single molecules that could eventually be switched or read with a device such as a scanning tunneling microscope tip. Among molecular magnets studied thus far, the lanthanide complex Er(trensal) has recently captured attention. This new class of trigonal, non-flat, single ion magnets (SIMs) offers spectroscopic access to ultrasharp 4f-4f transitions, opening up the possibility for optical manipulation of its magnetization and independent handles to study the electronic structure of individual molecules on surfaces.



To learn more about the behavior of Er(trensal) on substrates, Dreiser *et al.* (DOI: 10.1021/nn500409u) used a variety of methods, including X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, X-ray magnetic circular dichroism, scanning tunneling microscopy, and density functional theory calculations, to probe multilayer and monolayer coverage of Er(trensal) on Au(111) and monolayer coverage on a ferromagnetic Ni thin film on Cu(100). Results suggest that while Er(trensal) was loosely physisorbed on Au(111), with the easy axes randomly oriented, the SIMs were more firmly chemisorbed on the Ni/Cu(100), with chemical bonding between Er(trensal) and the Ni substrate. The authors suggest that their study paves the way for optical investigation, addressing, and control of large single magnetic moments on surface-deposited SIMs.