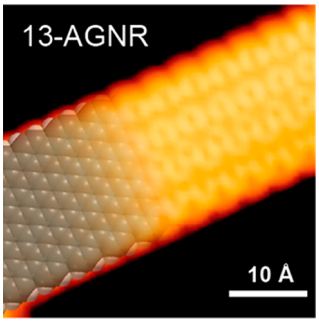
Minding Graphene Nanoribbon Band Gaps with Molecular Precursors

Graphene nanoribbons (GNRs) have captured attention with the unique electronic and magnetic properties that emerge from the various structures of these materials and depend on width, crystallographic symmetry, and edge structure. The ability to control these characteristics is essential for tuning the properties of these two-dimensional strips of graphene. In particular, armchair GNRs are thought to be especially promising toward device applications, with band gaps predicted to be inversely proportional to GNR width. However, the numerous top-down approaches used thus far to fabricate GNRs have provided only limited control over the ribbons' dimensions and symmetry. Bottom-up synthesis methods have shown some promise. Yet, choosing molecular precursors to yield the desired results remains challenging, with no GNRs with widths greater than $n = 7$ synthesized thus far with this technique.

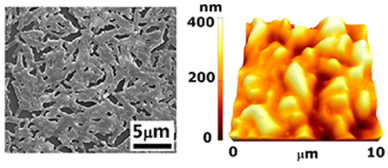
Hoping to overcome this limitation, Chen *et al.* (DOI: 10.1021/nn401948e) investigated a new type of molecular precursor. The researchers started with significantly modifying 10,10′-dibromo-9,9′-bianthracene (DBBA), a molecule used in previous studies. Radical step-growth polymerization and annealing yielded fully conjugated armchair GNRs with $n = 13$ (13-AGNR). Scanning tunneling microscopy and spectroscopy revealed that these new 13-AGNR have a band gap of 1.4 eV, significantly smaller than the band gap of 7-AGNR. Further examination revealed the existence of edge states associated with hydrogen-terminated sp^2-hybridized carbon atoms at the zigzag termini. The authors suggest that this new bottom-up fabrication method could pave the way toward new GNR-based nanotechnology.



Inactivated Cells Make an Impression

Cell imprinting is a recently developed technology for capturing and sorting cells. In this method, a polymer is cured around template cells that are subsequently removed, leaving behind cavities with structural and chemical information for recognizing target cells. Cell imprinting could prove particularly useful for biomedical applications that require rapid cell identification, such as in the diagnosis of dangerous, infectious diseases such as tuberculosis. However, using live cells for tuberculosis cell imprinting has several challenges. For example, live cells are fragile, which can harm the conformational integrity of the templates. They can also secrete factors that affect recognition of the polymer film, which then affects capturing selectivity. In addition, working with living cells comes with a risk of infection.

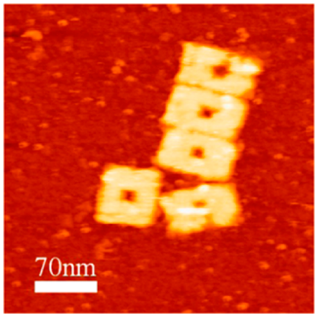
To circumvent these difficulties, Ren *et al.* (DOI: 10.1021/nn401768s) investigated using killed cells for cell imprinting. Using *Mycobacterium smegmatis* as a surrogate for *M. tuberculosis*, the researchers found that inactivating cells by various chemical methods and using these dead cells for cell imprinting greatly improved the capture selectivity when the captured cells were inactivated in the same way. Further examination showed that this selectivity, which was enhanced by a factor of 3, results from stiffening the cell surface through cross-linking of amine groups as well as eliminating chemicals secreted by the living cells. Beyond improving capture selectivity, cell inactivation comes with the additional benefit of removing the risk of working with a live pathogen. The authors note that these results, which readily translated to various strains of *M. tuberculosis*, suggest that using inactivated cells could be a better choice than live cells for cell imprinting.



DNA Origami Controls DNA Translocation

Synthetic silicon nanopores are a prominent example of nanostructures that require molecular control of shape and composition. Such control has already made these structures useful for label-free, single-molecule sensing. However, to increase their specificity and sensitivity to an increasing array of analytes, achieving even better control over their internal architecture and surface will be necessary. Fabricating silicon nitride nanopores can be challenging and time-consuming, requiring a transmission electron microscope or electron beam to ablate the surface. To get around these difficulties, researchers have instead used glass nanocapillaries as a substitute, recently combining them with DNA origami to make hybrid nanopores.

Taking this work one step further, the same team of Hernández-Ainsa *et al.* (DOI: 10.1021/nn401759r) developed hybrid nanopores in which the DNA origami can be applied and removed in a reversible and repeated fashion. The researchers designed flat, rectangular DNA origami structures with central nanopores of assorted sizes. After adding these nanopores to a reservoir containing the nanocapillary tips in a salt solution, adding a positive voltage trapped the DNA origami structures onto the nanocapillaries. Reversing the voltage effectively removed the nanopores. Tests showed that by tuning the pore size, the researchers could control the folding of double-stranded DNA as it passed through the pore. Additionally, by adding binding sites in the nanopore, the researchers could selectively detect single-stranded DNA as a function of its sequence. The authors suggest that these hybrid structures represent a simple way to create tailored nanopores with glass nanocapillaries and DNA nanotechnology.



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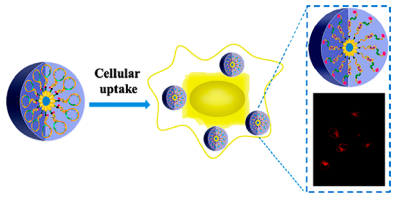
Sneaking Imaging Molecules into Cells

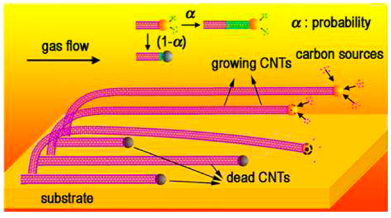
Understanding where biological molecules are inside cells, as well as how they move and interact, is critical for understanding normal physiological processes, disease states, and therapeutic targets. To that end, many nucleic acid molecular probes have been designed for intracellular imaging of proteins, RNAs, and small molecules. However, the use of these probes has proven challenging due to inefficient probe introduction and uneven distribution of probes inside cells. To solve these problems, some research teams have turned to nanomaterials to deliver nucleic acid probes into cells. However, nanomaterials can have cytotoxic effects.

To solve these problems, Wu *et al.* (DOI: 10.1021/nn402517v) developed switchable aptamer micelle flares (SAMFs) for intracellular imaging of biological molecules. These nanostructures are self-assembled from conjugates containing an aptamer switch probe, a PEG linker to a short DNA sequence that is complementary to the aptamer, and a diacyllipid tail. A fluorophore is attached to the 3′ end of the probe, and a quencher is attached between the 5′ end and the tail. With aptamers chosen for the biomolecule adenosine triphosphate as a proof-of-principle, the SAMFs were designed so that they stayed in a loop–stem structure in the absence of ATP in an "off" position, opening into an "on" position in the presence of the molecule. Tests showed that SAMFs entered cells more readily than aptamer switch probes without the external auxiliary. These new probes effectively sensed ATP, fluorescing in a dose-dependent fashion without cytotoxicity. The authors suggest that SAMFs show promise for molecular imaging in bioanalysis, disease diagnosis, and drug delivery.



Carbon Nanotubes Go Long

Carbon nanotubes (CNTs) are thought to be one of the strongest materials ever known. Their extraordinary mechanical properties make these one-dimensional cylinders of carbon promising candidates for superstrong fibers, bulletproof armors, and even cables for space elevators. Before these applications can become reality, researchers must determine how to mass-produce CNTs of macroscopic length. Thus far, gas-flow-directed chemical vapor deposition on silicon substrates has been the most effective method for producing ultralong CNTs. However, the longest CNT reported was only 20 cm. Moreover, the density of ultralong CNTs per batch remains very low, with number density decreasing as axial length grows. How to grow longer CNTs remains a pervasive question.

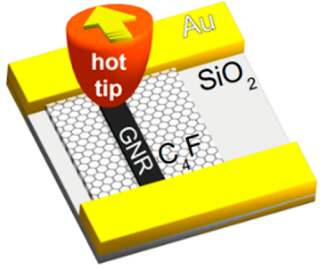


Seeking a way to increase CNT length, Zhang *et al.* (DOI: 10.1021/nn401995z) looked to the Schulz–Flory distribution, a mathematical function that typically describes the relative ratios of polymers of different lengths after a polymerization process based on their relative probabilities of occurrence. Using this function suggested that the most important parameter in growing ultralong CNTs is the probability that a catalyst particle keeps active enough to continue growing the CNT. Based on these findings, the researchers examined the role of a variety of factors known to be involved in influencing catalyst activity, including growth temperature, carbon feedstock, flow field, and space velocity. By optimizing these parameters and using a "furnace moving" method, the researchers were able to synthesize CNTs up to 55 cm. The authors suggest that the Schulz–Flory distribution sheds new light on the understanding and rational design of growing ultralong CNTs.

Producing Graphene Nanoribbons: It Is Written

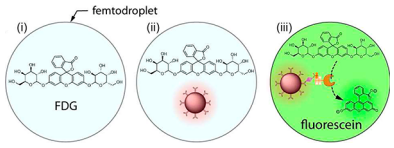
Graphene nanoribbons (GNRs) have been proposed as potential components for all-carbon nanoelectronics based on their ability to open a band gap due to size confinement and the potential for greater control over size and defined interconnectivity between GNR devices. Multiple methods have been suggested to produce narrow GNRs, including electron beam lithography (EBL), shattering exfoliated graphite by ultrasonification, unzipping carbon nanotubes and nanowires masks. However, each of these techniques comes with significant drawbacks that can affect performance, including low yield, contamination, defects, and rough edges. Other than EBL, none of these techniques provides a way to place GNRs precisely, yet EBL procedures generally damage GNR edges and leave residues on their surfaces. In addition, most lithographic techniques geometrically isolate GNRs by cutting them out of larger films, rather than the preferred method of chemical isolation, which stabilizes the GNR edges to prevent unintentional doping. Recently, researchers have had some success in using thermochemical nanolithography (TCNL) to produce GNRs, using a heated probe to reduce insulating graphene oxide directly to graphene ribbons. However, this method provides incomplete reduction, leaving some oxygen within the lattice.

Seeking more complete reduction, Lee *et al.* (DOI: 10.1021/nn4021746) used TCNL with graphene fluoride instead. Results show that this technique produced chemically isolated GNRs as narrow as 40 nm. Further examination indicated that these GNRs were p-doped, with low sheet resistances in air, only about 10 times higher than pristine graphene. The authors suggest that TCNL on graphene fluoride could be a promising technique for producing GNRs with tunable conductivity for electronic devices.



Better Immunoassays, Drop by Drop

The enzyme-linked immunosorbent assay (ELISA) has been the gold standard immunoassay since its development in the 1960s and early 1970s. This technique can detect biomarkers at concentrations above picomolar, but for diagnosing and tracking some diseases and cancers, detecting femtomolar concentrations is necessary. A promising solution recently developed for increasing ELISA resolution involves monitoring the turnover of a fluorogenic substrate within well-arrays containing single enzyme molecules in an assay mixture or encased in femtoliter water-in-oil droplets. However, the scalability and flexibility of this technique is inherently limited by the need to fabricate femtoliter wells mechanically. Microfluidics-based droplet platforms can



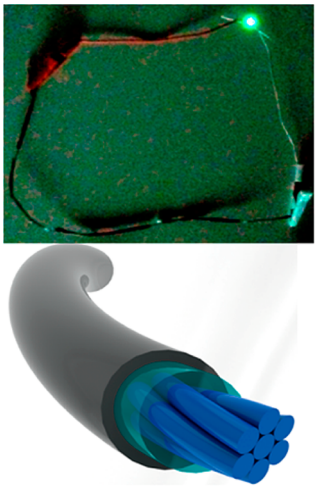
only generate highly monodisperse droplets on the pico- to nanoliter scale. At these volumes, it can take several hours of enzymatic activity to detect single enzyme molecules.

Working toward a better solution, Shim *et al.* (DOI: 10.1021/nn401661d) developed a method to generate and to manipulate highly monodisperse femtoliter droplets at the high frequency of 1.3 MHz. Their method involved generating a device with channels that simultaneously combined the substrate, proteins or beads, and oil. To generate a large shear force between the water and oil and low surface tension at the oil–water interface, the researchers introduced a flow-focusing nozzle into their device's design with a local constriction where all these channels met. As a proof-of-principle, the researchers used this system to detect low concentrations of prostate-specific antigen successfully. The authors suggest that further engineering to this system could increase its sensitivity.

A Thread Closer to Wearable Electronics

For wearable technology to become a reality, researchers must develop better fiber electronics or electronic capabilities on textile fabrics. Such textile electronics derive their capabilities from conducting and/or semiconducting materials built into textile fibers. Traditionally, metallic fibers have served as the core material to construct wearable supercapacitors. However, because these fibers have several disadvantages that make them unsuitable for textiles—including their tendency to oxidize under ambient conditions, poor bendability, and heavy weight—researchers have increasingly looked to a variety of other materials, including Kevlar fibers combined with ZnO nanorods, plastic fibers coated with gold and graphite nanoparticles, and carbon nanotubes and graphene fibers. However, these materials have had their own challenges, including low capacitance, low energy density, poor power density, and poor bendability.

Seeking to improve upon these earlier iterations, Le *et al.* (DOI: 10.1021/nn4016345) developed a coaxial fiber supercapacitor using all carbon materials. This new supercapacitor was constructed using a carbon microfiber bundle as the base, then spray-coated with multiwalled carbon nanotubes to form a central electrode. Around this, the researchers wrapped an electrospun carbon nanofiber film that served as an outer electrode. Tests showed that this coaxial fiber supercapacitor performed significantly better than other fiber supercapacitors developed to date, with a higher capacitance, energy density, and power density. Cyclic voltammetry showed that these properties changed little upon bending. The authors attribute this improved performance both to the supercapacitor's high surface area due to its coaxial structure and to its all-carbon construction with its high conductivity. They note that similar supercapacitors might eventually be used in textile electronics.



Lithiated Silicon's Phase Transition: Crystallizing Understanding

For next-generation rechargeable lithium ion batteries, researchers have proposed using silicon as an anode material. In this environment, silicon shows some unique behaviors. Upon lithiation, both crystalline and amorphous silicon transform to amorphous Li_xSi (a-Li_xSi), which subsequently becomes a crystalline compound as lithiation enrichment continues. Numerous studies have shown that highly lithiated a-Li_xSi crystallizes quickly and only to either $Li_{15}Si_4$ or $Li_{22}Si_5$, but researchers do not yet have an atomistic mechanism to explain this phenomenon. As this behavior can affect performance, understanding how and why this crystallization occurs could help investigators build better batteries.

Taking a detailed look, Gu *et al.* (DOI: 10.1021/nn402349j) used *in situ* scanning transmission electron microscopy, electron energy loss spectroscopy, and density functional theory calculations to investigate the transition of a-Li_xSi to crystalline $Li_{15}Si_4$. Their findings show that when the lithium concentration in the amorphous material reaches the critical value of $x = 3.75$, a-Li_xSi transforms to crystalline $Li_{15}Si_4$. The process appears to be solely controlled by the lithium concentration, with no large-scale atomic migration or phase separation taking place. Density functional theory suggests that crystalline $Li_{15}Si_4$ forms preferentially over other possible crystalline phases because its electronic structure is similar to a-$Li_{3.75}Si$. The authors suggest that more microscopy and spectroscopy work with high spatial and fast temporal resolution is needed to understand this phase transition.