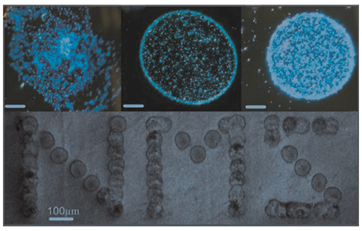
Graphene Electronics, Fresh from the Printer

Flexible electronics have the potential to revolutionize consumer products, with applications ranging from touch screens to electronic paper to electronic textiles. Thus far, researchers have created flexible electronics using two broad methods: either bonding substrates with field-effect transistors (FETs) to flexible plastic by transfer printing, or preparing FETs directly on target substrates. Inkjet printing is one way of accomplishing the latter method and has been used to prepare thin film transistors (TFTs) using organic conducting and semiconducting ink with "drop on demand" technology. However, these devices have mobilities that still average far lower than TFTs made of silicon.

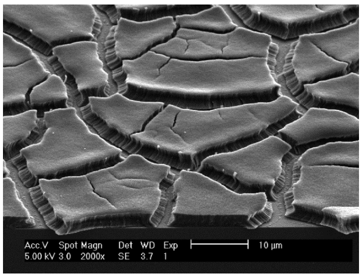
Pursuing a better TFT through inkjet printing, Torrisi *et al.* (DOI: 10.1021/nn2044609) developed an ink based on graphene, a material recognized for its outstanding electronic properties. To prepare their graphene ink, the researchers sonicated graphite flakes in *N*-methylpyrrolidone, a solvent with a high boiling point and heat of vaporization that generates high-yield, surfactant-free exfoliated graphite. Analyses showed that the resulting ink contained graphene flakes ranging from a single layer to a few layers and a few hundred nanometers across. The researchers applied these to various substrates and annealed them for a few minutes to remove the solvent, showing that substrates coated with hexamethyldisilazane (HMDS) yielded the most uniform and regular distribution of flakes. The TFTs printed on Si/SiO_2 using this method showed high mobilities, up to 95 $cm^2/V \cdot s$. The researchers also printed their graphene ink on borosilicate glass, creating patterns with high transparency and conductivity. The authors suggest that this method could be extended to develop inks with other layered materials to print hybrid heterostructures with novel properties.



Seeing the Nanotube Forest for the Trees

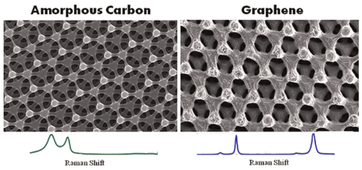
Single-walled carbon nanotubes' (SWNTs) interesting electrical properties make them a natural fit for a variety of future applications in consumer electronics. One possible use that has attracted a great deal of attention is the potential for SWNTs to replace copper as interconnects in integrated circuits since they are the only material thus far identified as capable of sufficiently high current densities. However, this application is only possible if SWNTs display interconnect resistances as low as copper's. To that end, a dense, parallel array of nanotubes will be necessary. Thus far, the densest SWNT forest grown is still too diffuse by a factor of ~30× for interconnect applications. Finding a way to increase SWNT area density is therefore an urgent goal.

In a new study, Zhong *et al.* (DOI: 10.1021/nn203035x) accomplish this goal by decreasing the diameters of individual nanotubes in forests to sizes far below those achieved through previous methods. The key to their strategy was designing a new catalyst. Although SWNT forests are typically grown using Fe/Al_2O_3 catalysts/support system, the newly designed catalyst sandwiches a thinner layer of Fe between a lower layer of sputtered Al subjected to a room-temperature O_2 plasma treatment and a top Al layer that becomes oxidized through air exposure. By combining this novel catalyst with a higher concentration of C_2H_2 along with a cold-wall chemical vapor deposition chamber, which allows rapid sample heating, the researchers achieved SWNT forests with an area density of 1.5×10^{13} cm^{-2}, the highest yet achieved. The authors note that this highly dense forest will ultimately be suitable for use as an interconnect in integrated circuits.



Graphene Goes 3D

Graphene's superior electronic, optic, and mechanical properties make it a natural fit for a variety of applications. However, graphene's two-dimensional (2D) structure limits its potential for many promising uses, including electrochemical transduction, gas-phase chemical sensing, and as an interface for many biological applications. Ideally, these products would translate graphene's 2D structure into a three-dimensional (3D) form.



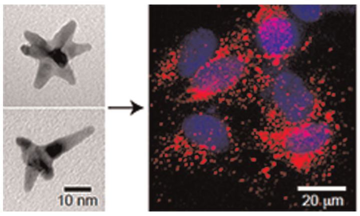
Toward this end, Xiao *et al.* (DOI: 10.1021/nn300655c) developed a method to create 3D porous graphene using predefined 3D pyrolyzed photoresist films. The researchers started by using interference lithography to craft amorphous porous 3D carbon structures composed of nanometer-sized arms and nodes arranged in a triangular in-plane structure. They sputtered these structures with Ni, then annealed them at a high temperature. Finally, the Ni was etched away in an acid solution. X-ray photoelectron spectroscopy showed that this method converted the predominantly sp^3 porous surface to sp^2 carbon. Raman spectroscopy results suggested that this final sp^2 structure consisted of multilayer graphene. Scanning electron microscopy showed that this structure was hollow, with wall thickness varying from 5 nm at the arms to 30 nm at the nodes. Tests showed that this 3D graphene had fast electron transfer processes, probably due to a combination of graphene's intrinsic high electron mobility, a high density of catalytic edge planes due to microscopically rough and crystalline graphene surfaces, and increased mass transport caused by the 3D structure. The authors suggest that these properties, combined with the structural versatility of their starting material, could make 3D graphene a promising material for new electrode applications.

10.1021/nn301587b

True Insight into How Nanoparticles Become Cancer Killers

■ The cell nucleus controls many important functions, including growth, proliferation, and apoptosis. These functions are also pivotal to the multiplication and spread of cancerous cells, making the nucleus a prime target for many cancer therapies. Since nanoparticles can easily enter cells, these materials have been exploited as promising drug-delivery vehicles. Nanoparticles loaded with drugs that potentially affect the cell nucleus have shown promise as anticancer therapies. However, the mechanism behind how they kill cancer cells remains unknown.

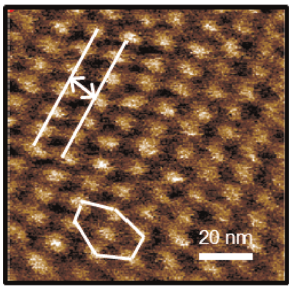
To investigate one potential nanoparticle-based therapy, Dam *et al.* (DOI: 10.1021/nn300296p) used microscopy to visualize what happened to the nucleus after treatment. The researchers synthesized Au nanostars loaded with AS1411, a DNA aptamer with a high binding affinity to nucleolin, a protein overexpressed in the cytoplasm of rapidly dividing cells that is known to traffic other molecules to the nucleus. Because AS1411 blocks several functions of nucleolin, this aptamer has shown promise as a chemotherapeutic agent. Confocal microscopy using fluorescent labeling suggested that these aptamer-loaded Au nanostars (Apt-AuNS) were picked up by nucleolin in HeLa cells and trafficked to the nucleus. Transmission electron microscopy showed that Apt-AuNS caused major changes in the nuclear envelope, causing deep invaginations and folds. The researchers were able to amplify this effect with femtosecond light pulses, which detach the aptamer from the AuNS surface once the nanoconstructs have entered cells. These changes to the nuclear envelope were correlated with increases in caspase 3 and 7 activity, indicating apoptosis, and a decrease in cell viability. The authors suggest that these insights might be used to improve nuclear-targeted cancer therapies.



“Blocking” Out a Strategy for Next-Generation Lithography

■ Immersion lithography using 193 nm wavelength light has already reached its predicted resolution limit of 36 nm. For next-generation integrated circuits, flash memory, and hard disk drives to be possible, researchers must develop new patterning technologies with even smaller features. Nanoimprint technology and electron-beam lithography have both shown success in the lab at replicating sub-36-nm features. However, both of these techniques face significant barriers for consumer applications. Block copolymers offer significantly less costly alternatives for nanoimprint template formation, but most of these systems have poor reactive ion etch selectivity between blocks, limiting designs to low aspect ratio features.

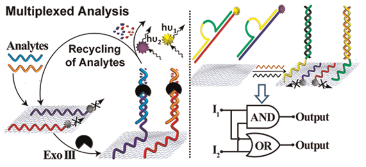
To get around these difficulties, Cushen *et al.* (DOI: 10.1021/nn300459r) developed hybrid diblock copolymers with natural and synthetic units. The researchers functionalized three different oligosaccharides with a single alkyne group, then joined these terminal groups to poly(*para*-trimethylsilylstyrene) (PTMSS) using azide–alkyne “click” chemistry. Solvent annealing the resulting products led to microphase separation, with well-ordered cylinders with feature diameters of about 5 nm evident on small-angle X-ray scattering (SAXS) studies. After spinning these block copolymers into thin toluene films, solvent and thermal annealing both produced well-ordered cylinders arranged in circular features and horizontal cylinder features visible using atomic force microscopy, suggesting that these materials lie on or close to a body-centered cubic sphere/hexagonally close-packed cylinder phase boundary. Further experiments showed high etch selectivity between the blocks, a characteristic pivotal for easy pattern transfer. The authors suggest that these block copolymers exhibit some of the smallest features reported to date in bulk and thin films, with features that make them promising materials for next-generation lithography applications.



Amplified DNA Detection: Feeling the Glow

■ Researchers have recently become interested in amplified DNA sensors and sensors for aptamers, or aptasensors. Several models for these devices have been developed, using various detection media and amplification machinery. Graphene oxide (GO) has shown promise as a substrate for such sensing applications because single strands of DNA readily attach to this material, but double strands do not. On the basis of this property, previous research has shown success in sensing single analytes using GO. However, the amplified detection of multiple analytes had not yet been demonstrated.

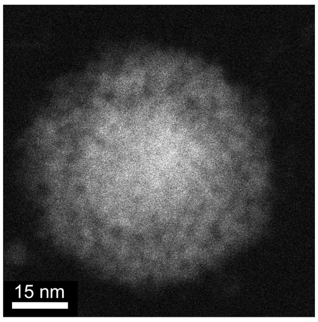
Showing that this feat is possible, Liu *et al.* (DOI: 10.1021/nn300598q) created a platform that provides amplified detection of two different DNAs or aptamers on a GO substrate. The researchers modified two different nucleic acid probes with different fluorophores, FAM and ROX. While unbound to target DNA, adsorption to the GO surfaces quenched these fluorophores. However, when the researchers introduced the target DNA strands, they dissociated from the GO and fluoresced. This signal was too small for detection. However, with the addition of exonuclease III, which digested the bound probe and released the target DNA, the signal amplified when the target bound subsequently with additional probes. After demonstrating that this system worked not only with the individual targets but with both at once, the researchers used a similar system to create a multiplexed aptasensor for thrombin and ATP. These investigators were able to enhance this platform further into a two-input logic gate that perform AND and OR functions. The researchers suggest that this simple and versatile system could be modified into multiple types of amplified DNA and aptamer sensors.



Watching Nanoparticles Form in Real Time

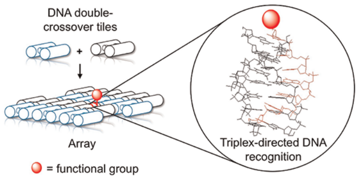
Because the properties of most nanomaterials vary greatly based on their dimensions and morphology, achieving precise control of these parameters is paramount to attaining desired qualities. One way to control the properties of a material better is to learn more about its growth mechanism. Typically, researchers have inferred details about nanostructure growth based on characterization after synthesis is finished through various microscopy techniques. However, such *post mortem* analyses might miss subtle but important steps that occur during the growth process. Some *in situ* gas studies have been performed, but these are not informative on the more common nanostructure syntheses performed in solution. The liquid studies that have been performed have not focused on fluids with complex rheology.

In a new study, Parent *et al.* (DOI: 10.1021/nn300671g) forge this missing link by performing direct *in situ* observations of mesoporous Pd nanoparticle synthesis in a highly viscous lyotropic liquid crystal template. The researchers first grew Pd nanoparticles from Pd salt on an *in situ* scanning tunneling electron microscope (STEM) stage in a surfactant template, first using the STEM beam as a reducing agent, with or without ascorbate as an additional chemical reducing agent. Time-lapse images and movies show initial growth through homogeneous nucleation, then continued growth of existing particles. Once particles reached a size of 10 to 15 nm, they became mobile, aggregating and trapping micelles from the template in the process. These observations confirm the utility of a STEM liquid stage for watching nanoparticle formation in real time, which the authors note could have implications for improving nanoparticle synthesis for a variety of applications.



DNA Nanostructures Hit a Triple

DNA is increasingly being used beyond biological applications, including the self-assembly of nanoscale objects and arrays. By taking advantage of Watson–Crick base-pairing rules, DNA strands can be designed to assemble into two- or three-dimensional structures. Complex assemblies often rely on reciprocal strand exchange between adjacent helices, called double-crossover molecules (DX), with large assemblies of these molecules known as tiles. Applications proposed for these intricate molecules usually rely on the incorporation of foreign molecules into the structure, including proteins, enzymes, and nanoparticles. These guest molecules are either chemically attached to one of the template oligonucleotides prior to assembly or recruited to another group and incorporated in the same way. However, the slow thermal annealing often required can damage heat-sensitive molecules such as proteins. Another strategy to accomplish the same goal is creating triplexes by adding a third strand onto double-stranded DNA. However, it has been unknown whether triplex-forming oligonucleotides (TFOs) can recognize specific loci within DX tiles and arrays.



To investigate, Rusling *et al.* (DOI: 10.1021/nn300718z) created several DX tiles with specific sequences included for designed TFO recognition. Electrophoretic mobility shift assay results showed that TFOs successfully targeted both the non-crossover strands and the crossover strands and, interestingly, the region spanning the crossover junction itself. By functionalizing the TFOs with biotin, the researchers were able to get visual confirmation that TFOs had successfully attached to DX tiles with streptavidin when viewing the resulting products with atomic force microscopy. The authors suggest that this approach could be useful for introducing a variety of other components into DNA nanostructures.

Nanoparticles Break on through to the Other Side

Researchers have become increasingly interested in resistive pulse analysis, a technique that allows detection, size measurements, or other assessments of solution-bound particles. Passing these items through a pore in a membrane between two reservoirs of ionic fluid causes a temporal and measurable change in the pore's electrical resistance. One promising application is DNA sequencing. Although researchers have successfully demonstrated that passing DNA through an engineered biological pore can distinguish the four bases, sequencing has not been possible since DNA moves through biological pores too quickly. An alternative is the use of alternate materials as nanopores, with graphene providing the necessary thinness for single-base resolution. However, researchers thus far have known little about the particle capture and translocation kinetics in such low aspect ratio pores and their influence on ion transport.

To learn more about these factors, Tsutsui *et al.* (DOI: 10.1021/nn300530b) investigated particle translocation in another solid-state pore with a low aspect ratio, formed in a sheet of Si_3N_4. Placing this membrane in an ionic solution of TE buffer composed of trishydrochloride and ethylenediaminetetraacetic acid (EDTA), the researchers observed as polystyrene beads of two sizes passed through the pore. This system successfully distinguished between the two bead sizes. Pore conductance scaled linearly with pore diameter, suggesting that access resistance, the resistance present on both sides of the pore, was the dominant mechanism behind ion transport. Further investigations showed that access resistance changed very little during particle translocation as long as multiple beads were not trapped in the pore. The authors suggest that the behavior of the solid-state Si_3N_4 nanopore could mimic that of graphene nanopores for resistive pulse analysis.