

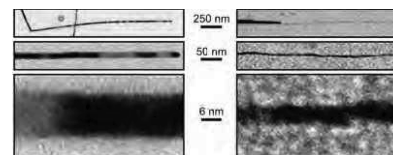
### Treating CdSe Nanowires as Individuals

■ Semiconductor nanowires have attracted increasing attention over the past decade due to their unique optical and electrical properties, which can potentially be exploited at the same time. Nanowires engineered with diameters below the Bohr radius may prove especially interesting for optical applications since the band gap of these materials depends on the diameter. Although measurements on ensembles of such thin nanowires have revealed intriguing properties, such as increasing absorption and photoluminescence peak energies with decreasing diameter, little is known about what properties may lie hidden in individual nanowires.

Seeking to separate properties inherent in single nanowires from those present in

assemblies, Myalitsin *et al.* (DOI: 10.1021/nn202199f) used a combination approach to examine how diameter affects the optical band gap in individual CdSe nanowires. After synthesizing nanowires with an average diameter of 11 nm, the researchers took atomic force microscopy (AFM) and scanning fluorescent microscopy images of what appeared to be a single nanowire. Transmission electron microscopy revealed that what appeared to be a single nanowire was really a bundle of three, highlighting the inherent difficulty in using AFM or photoluminescence alone to distinguish individual nanowires. The researchers also found that AFM overestimated the diameters of individual nanowires, potentially due to ligands still present on the nanowires' surfaces. Further

investigations comparing confirmed individual nanowires showed that the optical band gap strongly increases with decreasing diameter. The researchers note that these experimental results match some theoretical predictions but deviate from others. These findings emphasize the difficulty of studying individual nanowires and incongruities in current theoretical models.



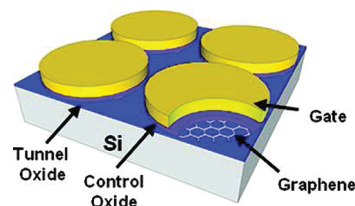
### Thanks for the Graphene Flash Memories

■ Flash memory is ubiquitous in a variety of electronic devices, ranging from personal computers to mobile phones. The most common type of this technology, known as floating-gate flash memory, encodes memory through a voltage pulse on a gate electrode, which allows electrons to pass through a tunnel oxide from a silicon channel to a semiconducting storage layer. Although this type of memory is currently considered the industry standard, it has intrinsic limitations that prevent increasing data storage as parent devices are miniaturized. As devices reduce in size, the gate-coupling ratio shrinks, and crosstalk increases between neighboring floating-gates.

In an effort to minimize these problems for floating-gate flash memory, Hong *et al.*

(DOI: 10.1021/nn201809k) looked to graphene. The researchers used chemical vapor deposition to grow sheets of single- and multi-layered graphene, then incorporated these sheets into floating-gate flash memory devices on the tunnel oxide surface. Electrical tests showed that devices crafted with multilayered graphene have a greater memory window—the threshold needed to switch from the 0 to 1 binary states—than do single-layered graphene devices, suggesting that charges responsible for the wide memory window are stored within the graphene layers. Additional measurements suggest that the graphene devices should lose only about 8% of their charge over a decade, making them practical for long-term use. Further examination indicates that the graphene's ultrathin nature effectively

reduces crosstalk between cells to negligible amounts, even at very small cell-to-cell distances. These findings suggest that graphene could be an instrumental part of flash memory as devices are miniaturized.

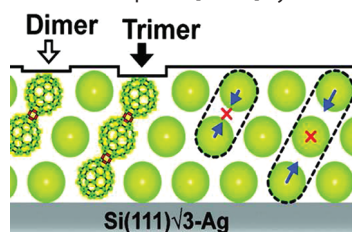


### Fullerene Molecules Work on the Chain Gang

■ One of nanotechnology's ultimate goals is creating nanoscale assemblies of molecules whose defined architectures in turn affect their properties. In that vein, some researchers have sought to achieve this objective using covalently connected fullerene  $C_{60}$  molecules, whose electronic, electrical, magnetic, and optical properties are controllable through bonding. Oligomers of up to three  $C_{60}$  molecules have been formed using methods including photoirradiation, high pressure and temperature, and alkali-metal doping. However, these methods are not able to control oligomer size precisely.

Seeking a new way to produce  $C_{60}$  oligomers, Nakaya *et al.* (DOI: 10.1021/nn201869g) used a strong electrical field and tunneling current produced by the tip of a scanning tunneling microscope (STM). The researchers prepared multilayer films of  $C_{60}$ . Placing the STM tip above the film surfaces, the researchers applied negative sample

bias voltages and tunneling currents of different strengths. Measurements after treatment showed that the surface-most molecules were displaced downward by small, but measurable, amounts. Tests showed that the stronger the tunneling current, the greater the number of  $C_{60}$  molecules that were covalently linked in a vertical pathway. The researchers also found that the thicker the  $C_{60}$  films, the longer the resulting oligomers. Further investigations suggest that the oligomerization is not a chain reaction, but rather a stepwise  $[2 + 2]$  cycloadditive



reaction, with greater tunneling current reaching deeper into the layers of  $C_{60}$ . By applying a positive sample bias voltage, the researchers show that the opposite reaction can also take place, decomposing the oligomers back into monomers. The researchers suggest that this controllable method could eventually be used to develop novel molecular electronics.

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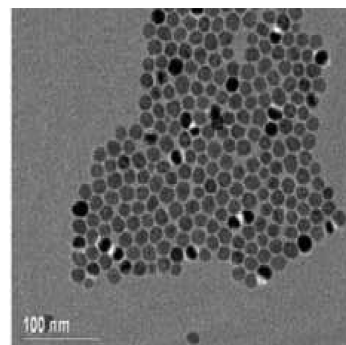
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### Probing for Mercury with Nanophosphors

Mercury's extreme toxicity makes it one of the most dangerous of the heavy metals, responsible for untold damage to the environment and health. Microbes easily convert the mercuric ion ( $\text{Hg}^{2+}$ ) into methylmercury, which builds up in the food chain and eventually collects in the bodies of humans and other animals, damaging the central nervous system. Finding a way to detect and to quantify  $\text{Hg}^{2+}$  is pivotal to focusing remediation efforts. Currently, fluorescent chemodosimeters are used most often to sense trace amounts of  $\text{Hg}^{2+}$ . However, these tools have critical limitations, such as inadequate penetration into biological tissues. The use of upconversion luminescence (UCL) has attracted increasing attention as a strategy for sensing and bioimaging that could avoid these difficulties. However, no UCL probes have yet been developed for  $\text{Hg}^{2+}$ .

In a new study, Liu *et al.* (DOI: 10.1021/nn202620u) developed a novel UCL system combining an upconversion nanophosphor (UCNP) with a  $\text{Hg}^{2+}$ -responsive ruthenium complex (N719). The complex, dubbed N719-UCNP, was prepared by ligand exchange of oleylamine-coated UCNP with N719. The prepared complexes were characterized by X-ray powder diffraction, transmission electron microscopy, energy-dispersive X-ray analysis, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Each method confirmed that N719 had successfully assembled on the UCNP surface. UV/vis absorption experiments showed that N719-UCNP successfully and specifically sensed  $\text{Hg}^{2+}$  in solution, changing the solution from red to orange. The same selective sensing capabilities were demonstrated in live HeLa cells, without the

complex itself causing toxicity. The authors suggest that this strategy could prove to be a useful way to detect  $\text{Hg}^{2+}$  in the environment and in biological tissues.



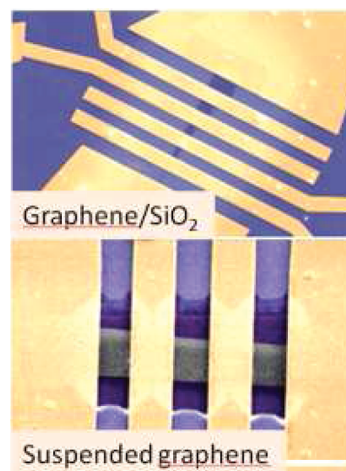
### Now Hear This: Low-Frequency Noise in Graphene Field-Effect Transistors

Graphene has attracted increasing attention for its potential in a range of applications, including a wide variety of electronics. In broadband circuits, intrinsic low-frequency noise limits their performance since it caps how small the input signal can be. Consequently, understanding low-frequency noise in graphene devices could help increase the signal-to-noise ratio and improve the performance of circuits. Various groups have been working to accomplish this goal using single- and multilayer graphene field-effect transistors, in which the noise generally follows a  $1/f$  frequency dependence. Findings have suggested that, in thin graphene nanoribbons, the gate-voltage dependence of noise follows Hooge's empirical relation. However, devices with widths in the hundreds of nanometers do not follow this relation, exhibiting complicated behavior. Suspended graphene, not on a

substrate, tends to have lower noise levels, but the reason is unclear.

Seeking to develop a more unified model to explain these previous results, Zhang *et al.* (DOI: 10.1021/nn202749z) performed a comparative study measuring the noise characteristics of graphene field-effect transistors using six on-substrate, nonsuspended graphene devices and five suspended graphene devices. Findings showed that noise amplitude away from the charge neutrality voltage followed a generalized Hooge's relation in which the Hooge parameter behaves not as a constant, but as a variable affected by scattering of charge carriers and the dynamics of scattering, which are sample- and temperature-dependent. The researchers suggest that the significantly lower noise in suspended graphene is due to higher carrier mobility. Consequently, suspended graphene could be a

promising option for low-noise electronics and sensors.



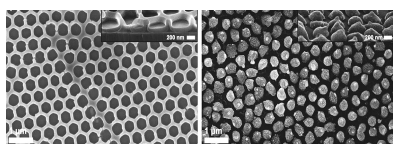
### Silicon Nanostructure Assemblies Spread Out

Silicon's abundance and compatibility with semiconductor processing technologies has led to the development of an extensive variety of silicon-based nanomaterials. These structures have been incorporated into photonic crystals, solar cells, and sensors, among other applications. Non-close-packed arrays of silicon nanostructures are also potentially useful due to their wide photonic band gap and possibilities for surface-enhanced properties. Researchers have already created non-close-packed

silicon nanostructures based on sacrificial inverse opal templates, but only in the amorphous phase (a-Si). Methods to create crystalline silicon (c-Si) nanostructures do exist but typically require several hours at elevated processing temperatures.

Seeking a new way to create non-close-packed silicon arrays in the crystalline phase, Tan *et al.* (DOI: 10.1021/nn2023446) developed a novel method that relies on pulsed laser irradiation. The researchers started by depositing a polystyrene colloid solution onto a substrate and overlaying it with  $\text{SiO}_2$ . Slowly calcining the resulting beads in hot air left behind a highly ordered hexagonal close-packed template. After filling the template with a-Si, the researchers used nanosecond laser pulses to melt this into c-Si.

Scanning electron microscopy images revealed the resulting non-close-packed arrays of teardrop-shaped c-Si. The arrays maintained excellent long-term order with uniform separations between particles. The size of these structures was tunable based on the size of the starting polystyrene beads. Additionally, the technique could be easily modified to create stacked layers of periodic structures. The authors suggest that this technique could eventually be adapted to create silicon nanostructures with diverse symmetries and unique properties for a variety of applications, such as sensors, catalysis, and energy conversion.

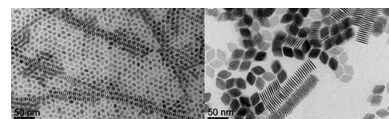


### Small-Angle X-ray Scattering Steps Up to the Nanoplate

■ For more than a decade, researchers have been investigating the intriguing properties of nanocrystal superlattices. Those utilizing anisotropic nanocrystals as building blocks allow substantial variation in design, with differing orientations and positional orders resulting in unique corresponding characteristics. Although various constructions have been achieved using nanorods and nanoplates, investigators have faced significant challenges in gaining systematic control of macroscopic orientation over large areas. To manage construction of ordered superlattices, detailed characterization of these assemblies' structural parameters, including symmetry, domain orientation, interparticle spacing, and degree of order, will be necessary.

Moving closer to that goal, Paik *et al.* (DOI: 10.1021/nn203049t) looked to small-angle X-ray scattering (SAXS) to characterize GdF<sub>3</sub> nanoplate superlattices. The researchers synthesized ellipsoidal and rhombic nanoplates, then assembled these into liquid crystalline superlattices by slowly drying a drop of nanocrystal suspension in a volatile solvent on glycol-type polar subphases. Transmission electron microscopy revealed two different orientations: the nanoplates either lay flat on the subphase, stacking into columns, or form lamellar structures, standing on the subphase edge-on. Using both in-plane and out-of-plane SAXS, the researchers found that columnar and lamellar phases coexist in the assembled structures, with extensive long-range order. Further

investigation suggested that the subphase is responsible for determining the superlattices' orientations. Those with lower dielectric constants, such as tetraethylene glycol and triethylene glycol, induce the formation of columnar superlattices, whereas those with higher dielectric constants, such as ethylene glycol, are more likely to produce lamellar ordering. The authors note that such insights could eventually contribute to producing tailored superlattices with desired characteristics.



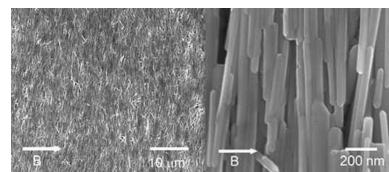
### Doped Semiconducting ZnO Nanowires Line Up

■ Theoretical advances have suggested that semiconductors in which a small percentage of atoms have been replaced by metal ions exhibit ferromagnetism at room temperature. These dilute magnetic semiconductors (DMS) could be extremely attractive components for spintronics, a class of devices that simultaneously exploit both electron spin and charge currents. Some researchers have speculated that spintronic devices could additionally exploit polarization-dependent optoelectronic properties if these DMS are fashioned into aligned arrays of nanowires. One potential way to produce these arrays is through chemical synthesis of large quantities of nanowires combined with bottom-up assembly by lyotropic ordering in fluid suspensions.

Bringing this idea to fruition, Zhang *et al.* (DOI: 10.1021/nn203070d) created aligned,

metal-doped ZnO nanowires using a combination of solvothermal synthesis and lyotropic ordering using mechanical shear and magnetic fields. The researchers first synthesized ZnO nanowires doped with small amounts of Mn and Co. UV-vis spectroscopy and electron paramagnetic resonance spectroscopy confirmed that these dopant ions were well incorporated into the nanowires. Superconducting quantum interference device magnetometry showed that both Mn- and Co-doped materials exhibit paramagnetism. By coating the nanowires with thiol ligands, the researchers were able to disperse them into organic solvents without significant aggregation. High concentrations led to the formation of a single phase with liquid crystalline order. Exposing these suspensions to mechanical shear produced highly ordered, dense arrays of nanowires.

For only the Co-doped nanowires, evaporation under a magnetic field also produced aligned arrays. The authors suggest that such lyotropic self-assembly has proven to be a useful strategy for fabricating aligned, doped nanowires, which could be useful for a variety of applications.

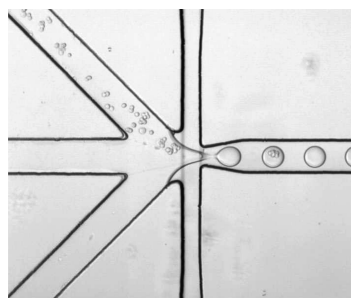


### Finding Cells in a Haystack with Microfluidics

■ Spotting atypical cells or enzymatic activity could be useful for biomedical research, diagnostics, or therapeutics. To this end, researchers recently developed an assay dubbed rolling-circle-enhanced enzyme activity detection (REEAD) to detect enzymatic DNA cleavage-ligation events at the single-molecule level. This technique relies on converting linear DNA sensors to circular products, which are isothermally amplified. These copies are in turn visualized by hybridization of fluorescent probes. In principle, this assay should be able to analyze events in single cells, though the original setup in a ~9 mm<sup>2</sup> area tends to result in spreading of signals.

To boost this sensitivity by reducing the setup's size, Juul *et al.* (DOI: 10.1021/nn203012q), who developed the original REEAD assay, incorporated microfluidics. The researchers

loaded one microfluidic channel with HEK293 cell populations mixed with different proportions of cells expressing Flp recombinase. Another channel carried a DNA sensor for Flp recombinase, and a third channel contained a lysis buffer to open the cells. These merged channels were broken up by an oil stream to form an emulsion with



picoliter-sized droplets. These droplets were individually captured in drop-traps, where rolling circle amplification occurred. This proof-of-principle experiment successfully identified the Flp recombinase-expressing cells, even at very small percentages in the population. Another experiment using probes for both Flp recombinase and human topoisomerase I at very sparse mixtures of cells per solution showed that this identification exercise was possible even at the single-cell level. The researchers suggest that this technique holds promise for elucidating rare cancer stem cells in a background tumor cell population.