

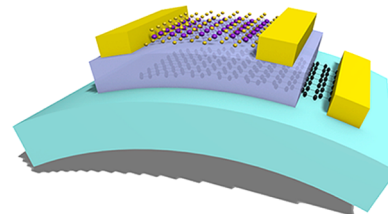
MoS₂ Field-Effect Transistors: Stacked for Success

■ As interest has steadily grown in graphene, many research teams have turned the spotlight on other two-dimensional materials, including insulating hexagonal boron nitride (hBN) and semiconducting molybdenum disulfide (MoS₂). The mechanical properties of MoS₂ give it promise for playing a pivotal role in flexible electronics. However, MoS₂ field-effect transistors (FETs) have shown only modest mobilities thus far. When these FETs are constructed with conventional dielectrics, such as SiO₂, performance suffers further due to low mobility and large hysteresis.

Seeking a way to incorporate MoS₂ into high-performance FETs, Lee *et al.* (DOI: 10.1021/nn402954e) built a stacked device using hBN as the dielectric and graphene

as the gate. The researchers mechanically stacked SiO₂ substrates first with few-layer graphene (FLG), followed by hBN, then a flake of MoS₂. Finally, the source, drain, and gate electrodes were patterned with electron-beam lithography and subsequent deposition of Ti/Au. These devices had low operating gate voltages, high field-effect mobilities, and a notable absence of hysteresis. Testing different thicknesses of the MoS₂ flakes, the researchers found that mobility increased with increasing numbers of layers. To harness this effect in transparent and flexible FETs, the researchers crafted devices with trilayers of MoS₂ on poly(ethylene naphthalate) substrates. These devices showed similarly low operating gate voltages, high mobilities,

and lacked hysteresis. This performance was virtually unchanged under applied uniaxial strains of up to 1.5%. The authors note that these stacked combinations could be used for a variety of flexible and transparent electronics that require low power consumption.



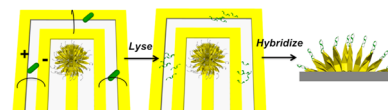
Building a Better "Bug" Zapper

■ To control and to manage infectious disease, investigators need a way to detect low levels of bacteria rapidly. Currently, no method exists that is both quick and sensitive. Culturing bacteria can take hours or days for samples to multiply into detectable levels. Methods that enzymatically amplify bacterial DNA, such as polymerase chain reaction, typically require a sample purification step that slows analysis. As an alternative to these methods, researchers have developed a wide array of chip-based molecular sensors to detect unique mRNA sequences. Although many copies of mRNA may exist in a single cell, providing natural signal enhancement, cells are

typically lysed in a separate chamber from where the sensor is situated, leading to a delay as lysate containing mRNA diffuses through solution.

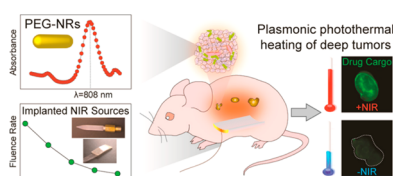
Seeking to address this issue, Besant *et al.* (DOI: 10.1021/nn4035298) developed a new device that uses electrochemistry to lyse cells less than 50 μm away from electrochemical nucleic acid sensors. In this system, electrodes surround a sensor, initiating lysis by producing hydroxide ions from water. This design allows large mRNA molecules to diffuse to the sensor within 10 min. On the sensor, a thiolated probe complementary to a unique portion of bacterial mRNA captures the nucleic acid

of interest, while an electrochemical reporter senses the change in electrostatics at the sensor surface, providing a signal. Tests showed that this new device effectively detected low concentrations of *E. coli* within 2 min of lysis. The authors suggest that lysing cells in close vicinity of the detector can significantly improve detection time and sensitivity.



Illuminating Plasmonic Cancer Therapeutics

■ Plasmonic nanomaterials' unique optical and electromagnetic properties have been exploited in a variety of medical applications. For example, these nanomaterials' ability to absorb specific wavelengths of light and to translate these to heat through the surface plasmon resonance effect has been used to ablate tumors locally, inhibit angiogenesis with milder heat damage, and enhance delivery of therapeutic cargoes. Many preclinical studies have investigated the use of poly(ethylene glycol)-coated gold nanorods (PEG-NRs), which have advantageous qualities including long-term stability, minimal cytotoxicity, and tunability to absorb specific wavelengths of near-infrared (NIR) light. However, NIR light delivered through external sources has limited penetration through biological tissue, limiting the use of these PEG-NRs to superficial tumors.



In a new study, Bagley *et al.* (DOI: 10.1021/nn4033757) develop a new strategy to combine systematically delivered PEG-NRs with locally implanted NIR light sources. Through initial computational modeling efforts, the researchers compared the performance of various silica rod designs joined with a NIR laser source with fiber optic meshes consisting of sub-millimeter fibers encased in adhesive medical-grade silicone. On the basis of these results, they chose to pursue silica rod designs. Testing this design in an orthotopic mouse

model of ovarian cancer, the researchers implanted it into the abdominal cavity of animals pretreated with PEG-NRs or untreated controls. Thermal profiling and histological analysis showed that the implanted device selectively heated the nanorods while avoiding heat damage to nearby organs. Additional experiments showed that this system could effectively enhance delivery of doxorubicin liposomes. The authors suggest that similar light-delivery systems could eventually play an important role in cancer therapeutics.

Published online September 24, 2013
10.1021/nn4047259

© 2013 American Chemical Society

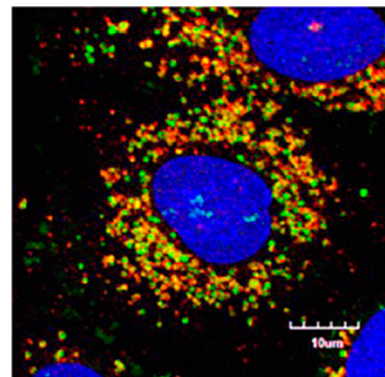
Breaking the Cycle with Amino-Modified Nanoparticles

While many types of nanoparticles can accumulate in cells with minimal toxicity, others can readily induce cell death. In this latter category are some positively charged polymeric nanoparticles, including amino-modified polystyrene nanoparticles (PS-NH₂). Once internalized, these particles collect in the lysosomes, causing swelling and membrane damage. This damage leads to leakage of proteolytic enzymes into the cytosol, triggering a cascade that causes changes in the cell cycle, inflammation, and cell death.

In a new study, Kim *et al.* (DOI: 10.1021/nn403126e) show that apoptosis is not inevitable. When the researchers administered a sufficiently low dose of PS-NH₂ to cells, the cell cycle was arrested without causing cell death. Using lung cancer epithelial cells as a model,

the researchers exposed these cells to various doses of PS-NH₂ or PS-COOH, a similar nanoparticle that has been shown not to cause cytotoxic effects. At high concentrations, the PS-NH₂ nanoparticles promptly killed cells. However, for PS-NH₂ concentrations lower than 100 μg/mL, cell proliferation significantly slowed and then appeared to stop, yet these treated cells did not die. Further investigation suggests that low PS-NH₂ doses interfere with the cell cycle, potentially halting progression at the G1/S checkpoint. These cells maintained consistent levels of ATP and continued to collect nanoparticles, suggesting that cell metabolism remained normal despite the effects on the cell cycle. In contrast, the PS-COOH nanoparticles caused no ill effects to cells or the cell cycle, regardless of dose. These results, the authors say, show the potential for

different types of nanoparticles, and even different dosages of the same nanoparticle, to cause different effects in cells.



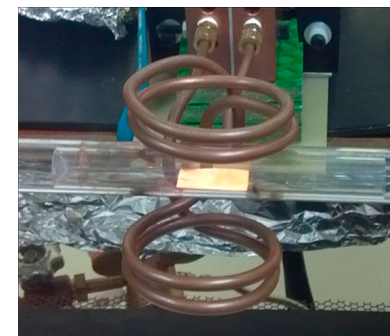
Cool New Method for Graphene Synthesis

The recent discovery that single-layer graphene can grow in large areas on the surface of copper foils finally opened the door to creating very large sheets of high-quality graphene, greatly expanding the potential applications for this material. However, commercial production of very large area graphene is still limited by some practical concerns. Although large ovens exist to synthesize this material, using such large volume ovens just to heat a thin metal foil is very energy inefficient. One alternative to this scenario is using radio frequency (rf) magnetic fields to heat the metal directly. This method has a host of advantages, including substantial energy savings, keeping the reactor walls cool and thus reducing thermal breakdown of

reactant gases, a faster rate of metal heating and cooling, and the ability to use glass or quartz reaction chamber walls to monitor the reaction in progress.

In a new study, Piner *et al.* (DOI: 10.1021/nn4031564) tested whether graphene would grow using rf-heated metal substrates. The team built a reactor with a gas injection system and rf heating. The copper foil substrate was inserted into a quartz tube. Outside the tube, the rf coil heated only the copper foil through induction. Using this system, the researchers produced graphene of similar or better quality than that synthesized through chemical vapor deposition. Tests in back-gated field-effect transistors showed that this graphene had high carrier mobility. The

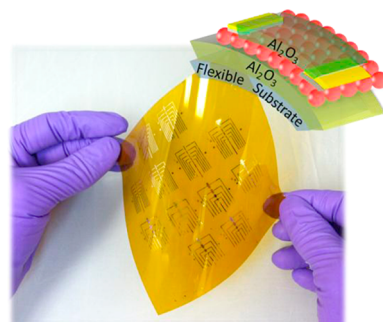
authors suggest that rf heating can produce high quality large area graphene with significant advantages over hot wall reactors.



Nanocrystal Films, Heal Themselves

Colloidal semiconductor nanocrystals (NCs) have unique, size-dependent electronic properties that make them an attractive material for use in electronic and optoelectronic solid-state devices. Using these materials has led to several record device performances in academic and industrial laboratories, but NCs are not yet in commercial use because they are not yet compatible with large-area, low-cost fabrication technologies. Colloidal semiconductor nanocrystal films are sensitive to air and solvents, limiting their fabrication to nitrogen gloveboxes and dry processes.

Seeking a solution to this conundrum, Choi *et al.* (DOI: 10.1021/nn403752d) synthesized NC films that have the ability to repair themselves with the aid of an *in situ* thermally triggered recovery agent. The researchers spin-coated thin films of CdSe NCs and annealed them, then thermally evaporated



indium metal onto the film and reannealed. Indium improved device performance, increasing mobility, lowering subthreshold swing, and reducing hysteresis compared to devices annealed without indium. When these devices were exposed to air, performance suffered, but high performance could

be recovered by reannealing at 200 °C for 5 min. Incorporating these indium-altered NC films into field-effect transistors produced similar deficits in device performance after exposure to air and several solvents commonly used in standard photolithographic processing. However, reannealing again restored high performance. As a final test, the researchers incorporated the hardy NC films into a series of wafer-scale integrated devices using photolithography and atomic layer deposition encapsulation. These devices were able to operate stably in air long-term. The authors suggest that such *in situ* recovery opens the possibility of low-cost, large-scale fabrication of NC device technologies.

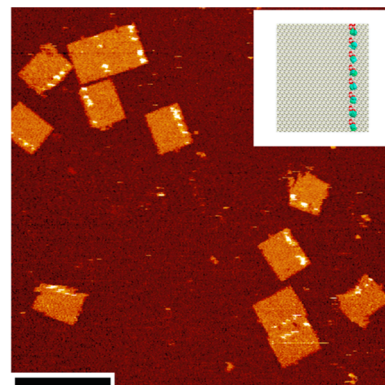
DNA, Protein, and the Ties That Bind

Efficiently binding DNA to other biomolecules is key to the developing field of DNA nanotechnology, which harnesses the well-studied self-assembly of DNA to produce nanoscale structures with designed shapes. Although DNA can be fashioned into a diverse array of structures, these structures lack the chemical and structural diversity found in other biomolecules, such as proteins. Consequently, attaching proteins to DNA to augment its properties can expand the range of functional applications for these nanostructures. Although protein–DNA hybrids could prove particularly useful, production of these combined structures remains challenging because of the low efficiency of conjugating proteins and other polymers to DNA.

Seeking to change the current paradigm, Sørensen *et al.* (DOI: 10.1021/nn403386f) developed a versatile and efficient way of

ligating polymers, proteins, and other biomolecules to DNA. Their method centers around the enzyme terminal deoxynucleotidyl transferase (TdT), used in native cells to add *N*-nucleotides to exons in immature immune cells. Deoxynucleotidyl transferase can also accept nucleoside triphosphates tethered to large biomolecules as substrates, as well as direct the ligation of biomolecules to the 3' end of native oligodeoxynucleotides. The researchers used this enzyme to tether DNA to five different macromolecules of different structural classes that are all used commonly in DNA nanotechnology and drug delivery and are activated by nucleoside triphosphates. These reactions proceeded rapidly and nearly to completion at low concentrations. With this method, the researchers used oligonucleotides labeled in parallel to produce nanopatterned DNA origami struc-

tures. The authors suggest that this method is a rapid and versatile way to incorporate non-DNA elements into DNA structures.



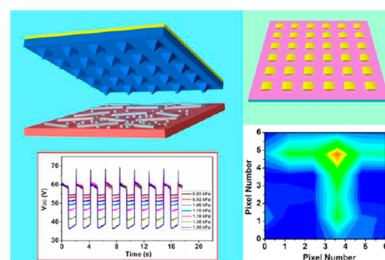
A Touch of Triboelectric for Tactile Sensing

Tactile sensing research has applications in a variety of areas, including artificial skin, flexible electronics, human–electronics interfacing, and microelectromechanical systems. Existing sensors typically work by pressure inducing a change in sensor properties, such as conductance, capacitance, or optical transmittance, with field-effect transistors as the read-out elements. However, one limitation of most current tactile sensors is that they rely on an external power source to work.

In an effort to develop a novel, self-powered sensor, Lin *et al.* (DOI: 10.1021/nn4037514) looked to the triboelectric effect, which couples contact electrification with electrostatic induction. The researchers created a polydimethylsiloxane membrane micropatterned on one side with pyramid structures through

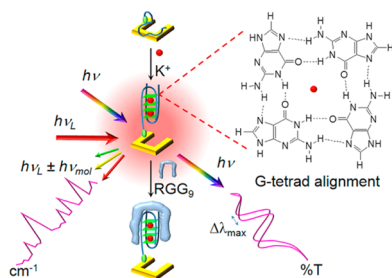
photolithography and templating. Touching the patterned side of this membrane, the researchers placed a piece of Al, its surface roughened by a composite of Ag nanowires and nanoparticles. Both surfaces were designed to increase contact between the two when the device was under pressure. Read-outs from attached electrodes showed that open-circuit voltage along with the amount of transferred charge density could be used to detect static pressure, and the short-circuit peak could be used for dynamic pressure monitoring. Tests showed that this device provided high sensitivity, fast response and relaxation times, long-term stability and reliability over tens of thousands of cycles, and a low detection limit. By incorporating multiple sensors in an array, the researchers were able

to use this self-powered device to monitor and to map applied local pressure distributions. The authors suggest that this device could be used for a variety of applications, including signature recognition or electronic skin.



Seeing Biomolecules in a New Light

Life-sustaining activities rely on the folding and binding of biomolecules. Consequently, developing a comprehensive understanding of biomolecules' conformational states, expressions, and binding processes is crucial for several different fields, including genomics, functional proteomics, clinical diagnosis, and disease treatment. Label-free surface plasmon resonance and localized surface plasmon resonance biosensors can provide quantitative information, binding affinity, and kinetic rates from molecules that change the local refractive index. However, these tools are not able to determine conformations or identify unknown molecules. Plasmonic biosensors based on surface-enhanced Raman scattering can detect conformational changes. However, surface-enhanced Raman scattering (SERS) suffers from several limitations, including



poor reproducibility of substrates and dependence on proximity and orientation of biomolecules with the substrate.

Seeking a new way to gather this information, Cao *et al.* (DOI: 10.1021/nn401645t) fashioned substrates with arrays of metamaterials, or split-ring resonators (SRRs). These SRRs provide two transducing channels to acquire

optical transmission data and SERS spectra of biomolecules in parallel. As a proof-of-principle, the researchers used this system to probe G-quadruplexes, showing that it is possible to investigate the conformational state and binding affinity of these biomolecules simultaneously in different environments. Additionally, the researchers also used this system to fingerprint and to detect a domain of nucleolin, a cancer biomarker that specifically binds to G-quadruplexes. The authors suggest that such metamaterial arrays could provide reliable, reproducible, and label-free analysis for a variety of fundamental and biomedical applications.