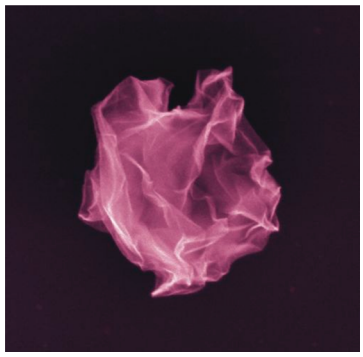
## Graphene "Paper Balls" Crumple the Competition

Future applications of graphene will require significantly increased production of this unusual material. However, methods of manufacturing graphene at large scales have suffered from its tendency to aggregate due to strong van der Waals attractions. Aggregated sheets do not disperse well in solution, and they have impaired optical and electrical properties because their accessible surface area is compromised. Although several strategies have been developed to prevent aggregation in solution, such as reducing sheet size and employing dispersing agents, graphene sheets often aggregate as they dry and become difficult to redisburse in solution.

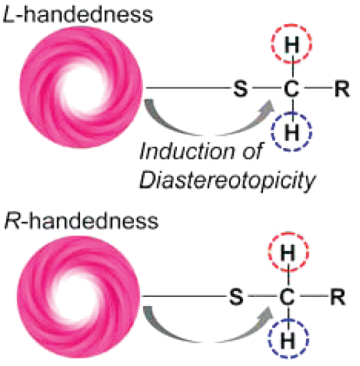
Trying a new tactic, Luo *et al.* (DOI: 10.1021/nn203115u) developed a method that crumples graphene sheets into balls that resist aggregation both in and out of solution, leaving their surface areas and useful properties intact. The researchers aerosolized an aqueous dispersion of micrometer-sized graphene oxide sheets, running individual droplets through a hot tube furnace. Rapid evaporation compressed the sheets into crumpled, submicrometer-sized balls. Scanning electron microscopy showed that the crumpled balls retained their morphology through a variety of processing conditions, including solution processing, thermal shock, microwave heating, and hydrazine treatment. Further examination suggests that the balls' robustness is due to strong $\pi-\pi$ stacking at their bent ridges. The crumpled balls withstood pelletization at 55 MPa, easily redisbursing in solvents with hand shaking, and retained their high surface area. As a proof-of-concept, the researchers showed that crumpled graphene used as anodes in microbial fuel cell electrodes outperformed graphene sheets. These findings suggest that crumpled graphene balls could hold considerable advantages over traditional graphene sheets for future applications.



## As the Gold Nanocluster Turns

Au nanoclusters can exhibit chirality, so they are particularly appealing for enantioselective and stereoselective catalysis. There are two ways to produce chiral Au nanoclusters: either through attaching chiral ligands to nonchiral Au nanoclusters or by preparing intrinsically chiral Au nanoclusters with a chiral metal core. Verifying the chirality of the metal core has been a long-standing challenge. Though circular dichromism has proven to be a useful method for probing chirality in individual nanoclusters, it produces a net zero signal in racemic mixtures.

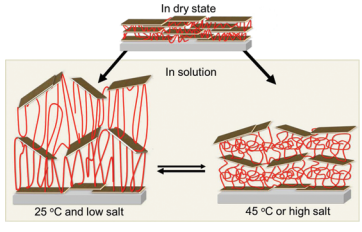
Seeking a method to identify chirality in mixed collections of chiral Au nanoclusters, Qian *et al.* (DOI: 10.1021/nn203113j) looked to NMR spectroscopy. The researchers used chiral $Au_{38}(SCH_2CH_2Ph)_{24}$ and nonchiral $Au_{25}(SCH_2CH_2Ph)_{18}$ as model systems. NMR spectroscopy results showed that the two germinal protons in each $CH_2$ group in the ligands delivered distinct signals, suggesting that these two protons are not chemically equivalent. For the $CH_2$ group closest to the chiral core, the researchers observed a chemical shift difference of up to 0.8 ppm. This effect, known as diastereotopicity, was absent in the nonchiral Au clusters, which displayed no chemical shift difference between the two germinal protons. When nonchiral Au nanoclusters were capped with chiral ligands, the researchers again observed diastereotopicity in nearby $CH_2$ groups. However, this effect appeared to result from their proximity to the chiral centers of the ligands themselves, not the chiral core. The researchers suggest that using NMR spectroscopy to detect diastereotopicity can be a reliable way to identify chirality in Au nanoclusters, even in racemic mixtures.




## Clay-Containing Layer-by-Layer Films: Just Swell

Over the past two decades, researchers have increasingly explored the advantages of adding clay—an abundant, inexpensive, and environmentally friendly material—to polymer films. In layer-by-layer (LbL) films, clay significantly enhances strength, while polymer constituents maintain flexibility. These clay-containing LbL films have been suggested as flame-retardants or anticorrosion coatings due to their exceptional oxygen-barrier properties. However, although all-polymer films have been explored as membranes for filtering and separating molecules in solution, LbL films containing clay remain untested.

To investigate their potential for use as filters under various conditions, Zhuk *et al.* (DOI: 10.1021/nn202812a) constructed LbL clay-containing films using poly(*N*-isopropylacrylamide) (PNIPAM) as the polymer base. Immersed in a slightly basic phosphate buffer solution, films 400 layers thick took up large amounts of water, swelling to be 14.5 times larger. Raising the temperature of the solution or, alternatively, increasing salinity decreased this swelling by about 40%. Swelling and deswelling were reversible, with films intact after multiple cycles. Spreading films onto 100 nm pore size polycarbonate membranes, the researchers tested their permeability to a fluorescent dye and fluorescently labeled dextrans of various molecular weights. Results showed that, with increased temperature, deswelling restricted access to the molecules with larger molecular weights. By adding a weak polyacid to the clay/PNIPAM LbL films, the researchers endowed pH-responsive properties. In solutions with higher pHs, these films swelled to about eight times their dry thickness. Permeability changed accordingly, with films becoming increasingly less permeable at lower pH. The findings suggest that these "smart" clay/polymer films could have numerous applications for separation, such as in microfluidic or biomedical devices.

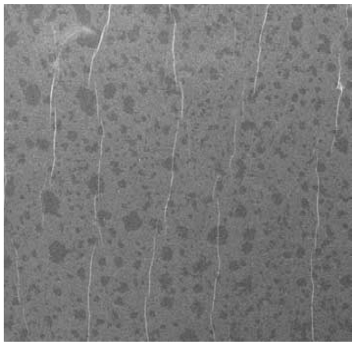



**Published online November 22, 2011**
**10.1021/nn204180j**

## Porous Graphene: A Holey Grail for Electrodes?

Graphene sheets' unique properties hold significant promise for a variety of electronics applications, including battery and supercapacitor electrodes. Their extraordinarily high in-plane conductivity and strength have the potential to enable more creative electrode designs, and their flexibility lends itself to exceptional durability through the large volume variations of charge/discharge cycling. However, the sheets' large aspect ratios present a drawback. As they dry, graphene sheets stack in aggregates joined together by strong van der Waals forces, limiting the circulation of electrolytes between layers and eliminating the positive effects of graphene's high surface area. Some groups have sought to solve this problem by creating vertical graphene stacks with many exposed edge planes and enlarged interlayer spacing. However, these designs proved fragile and labor-intensive to fabricate.

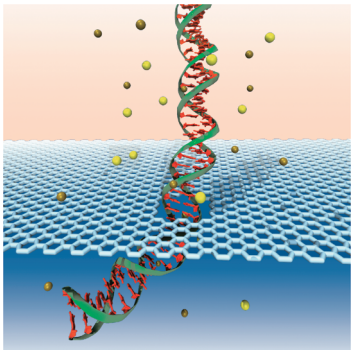
Seeking a better design, Zhao *et al.* (DOI: 10.1021/nn202710s) developed a method that introduces pores in graphene sheets, greatly expanding the material's accessible volume. The researchers' method punches holes in graphene using a wet chemical method that combines ultrasonic vibration and mild $HNO_3$ oxidation. Using four different concentrations of $HNO_3$, they created four different species of holey graphene. Scanning electron microscopy revealed sheets with increasingly larger holes with higher concentrations of $HNO_3$, ranging from 7 to 600 nm in diameter. Examination with X-ray diffraction suggested a reduced van der Waals attraction between holey graphene layers reduced in Ar or $Ar/H_2$ gas. Incorporated into electrodes, the holey graphene showed significantly less degradation upon repeated cycling, as well as enhanced Li-ion diffusion. The authors note that their novel holey graphene could significantly improve graphitic electrodes.



## Threading DNA through the Nanopore Needle

Recent findings suggest that nanopores could hold promise for single-molecule detection. As different molecules in ionic solution pass through the pore, variations in molecular size block the pore to different extents, resulting in different amplitudes and durations of ionic current blockades. This potential also extends to DNA. In principle, nanopores could differentiate the four nucleotides, A, T, G, and C, suggesting that this tool could form the basis for a novel high-speed sequencing method. Although DNA has been translocated through graphene, a material whose thin nature might accommodate individual base pairs, velocities were too high to permit adequate resolution.

To gain more insight on the kinetics of DNA passing through graphene nanopores, Sathe *et al.* (DOI: 10.1021/nn202989w) ran a series of all-atom molecular dynamics

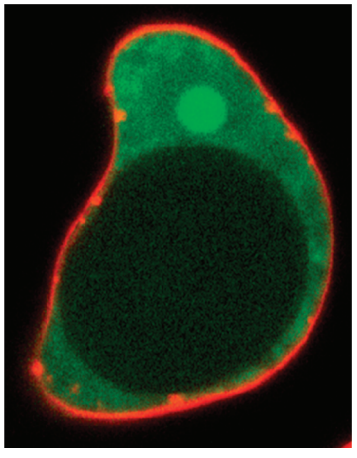


simulations. Placing a 45 base pair double-stranded DNA molecule at the mouth of a 2.4 nm graphene nanopore, the researchers investigated the effects of voltage variations on DNA translocation. Results showed that DNA blocks the current more effectively at lower bias voltages. As the voltage increased, the molecule elongated, allowing more ions to pass through the pore. Lower bias voltages, as well as negatively charged pores, also slowed DNA's journey, causing the molecule to stick to the graphene membrane and partially unzip. Simulations for DNA in a folded conformation showed a characteristic double-plateau current signature. Further simulations suggest that individual base pairs can indeed be successfully discriminated in nanopores in ultrathin graphene membranes. The authors note that understanding these different scenarios could eventually guide the development of nanopore-based DNA sequencing devices.

## Peering into Plant Cells with Single-Walled Nanotubes

Researchers have made many significant advances in understanding various aspects of plant biology in the last several years. However, several areas remain poorly understood due to a lack of useful tools to visualize plant cell interiors and organelles. For example, membrane trafficking and vesicle transport study has been limited because existing dyes are membrane-impermeable. This research has been similarly hampered by a lack of organelle-targeted molecular delivery agents.

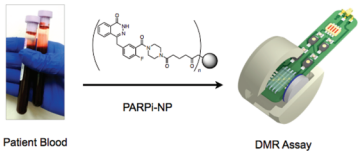
Hoping to advance plant cell biology, Serag *et al.* (DOI: 10.1021/nn2035654) developed a new visualization tool based on single-walled carbon nanotubes (SWCNTs). Because the diameters of individual SWCNTs approach the size of biomolecules, these materials could potentially be observed participating in subcellular processes if labeled with a functional tag. The researchers achieved this goal by labeling short carboxylated SWCNTs with the fluorescent dye fluorescein isothiacyanate. When the researchers incubated *Catharanthus roseus* cells with the modified SWCNTs (SW-F) or with just the dye, fluorescence after photobleaching (FRAP) tests showed that the SW-F accumulated preferentially inside cell vacuoles. After inhibiting carrier-mediated transport with probenecid, the SW-F remained in the cytoplasm, suggesting that the dye tag was necessary for subcellular distribution of the nanotubes. Further observation showed that, when SW-F entered the nucleus, the dye was eventually released from SWCNT surfaces. By experimenting with various conditions, including increasing or decreasing the medium pH and adding Exo1, a vesicle-mediated transport inhibitor, the researchers were able to control intake, location, and expulsion of SW-F. The findings suggest that SWCNT-based tools hold a viable place for improving visualization of processes in cells, potentially improving the understanding of plant biology.



## Hitting the Target with Diagnostic NMR

Nanomaterials are currently used for a variety of biomedical diagnostic and analytical applications. Typical applications have thus far included detecting whole cells, pathogens, soluble protein markers, or metabolites by using antibodies as affinity ligands. However, an area that remains relatively unexplored is using nanomaterials to assay drug–target binding quantitatively in clinical samples. Such a tool could help doctors tailor treatment decisions at the point of care, such as whether a particular drug or dosage is the best choice for an individual patient.

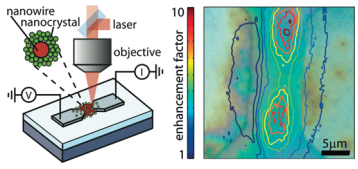
Seeking to capitalize on advances in portable diagnostic NMR, Ullal *et al.* (DOI: 10.1021/nn203450p) developed a new assay for drug–target interactions using a small-molecule drug attached to magnetic nanoparticles. The researchers used poly(ADP-ribose) polymerase (PARP) inhibition as their model system because several drugs in this category have made significant headway in trials for ovarian and breast cancer. After conjugating PARP inhibitor AZD-2281 to magnetic nanoparticles, the researchers found that they retained significant PARP inhibitory activity. Further tests showed that the conjugates' affinity to nuclear targets correlated with levels of PARP expression in various cell lines. These modified nanoparticles also provided an accurate readout of target inhibition in tests comparing five different commercially available PARP inhibitors. Trying the conjugates in a more clinically relevant setting, the researchers found that the conjugates successfully bound to scant numbers of ovarian and breast cancer cells spiked into whole human blood. The findings suggest that drug–magnetoparticle conjugates could form the basis for new target-binding assays, which would be useful for a wide variety of biomedical applications.




## Photodetector Nanocrystals Add a Line

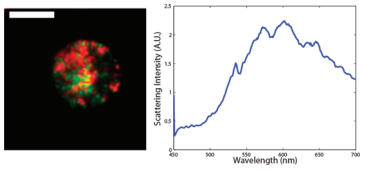
Semiconductor nanocrystals with controllable shapes and sizes are now available for a wide variety of applications due to recent advances in synthetic methods. These materials, with their tunable effective band gaps, are an attractive solution toward improving photodetector technologies. However, although various groups have successfully incorporated these materials into photodetector designs, nanocrystal solids and thin films typically exhibit low carrier mobilities, limiting their usefulness.

In an effort to improve charge carrier mobilities in these devices, Dorn *et al.* (DOI: 10.1021/nn203227t) created hybrid devices that combine CdSe/CdS nanocrystal films with embedded CdSe nanowires. The researchers first produced the CdSe nanowires using an electrically controlled solution liquid solid growth process, a method that allowed the nanowires to grow directly between metal electrodes on a substrate. They then dropcast colloidal CdSe/CdS nanocrystals synthesized using standard wet chemistry techniques. Using a scanning confocal microscope to illuminate the finished device locally, the researchers found strong enhancement in the generated photocurrent at 514 nm, a wavelength at which excitons were generated in both the nanocrystals and nanowires. Further investigation suggested that this boost was due to the nanowires enhancing exciton extraction from the nanocrystals by at least 2–3 orders of magnitude. The researchers suggest that devices based on this concept could be customized using other material combinations to detect specific wavelengths of light. Furthermore, since many types of particles create excitons when they interact with matter, the researchers suggest that this design could be modified to detect types of radiation other than photons.




## Nanoparticles Come Together for Receptor Dimerization

The human epidermal growth factor receptor 2 (HER-2), which plays a key role in cancer-related behaviors such as regulating cell proliferation, differentiation, survival, mobility, and adhesion, forms dimers upon growth factor ligand binding. In cells with high HER-2 expression, these receptors undergo constitutive homodimerization. The ability to observe this dimerization may eventually help identify signaling pathways that could be important targets for various cancers in which HER-2 is thought to play a role, including breast and ovarian cancers. Although several methods exist to observe receptor dimerization, including co-immunoprecipitation, chemical cross-linking, and fluorescent resonance energy transfer, each has drawbacks that severely limit its use.




Seeking a better way to observe this phenomenon, Crow *et al.* (DOI: 10.1021/nn201451c) relied on Au plasmonic nanoparticles. The researchers conjugated Au nanoparticles to HER-2 antibodies then incubated these modified particles with two human cancer cell lines: SK-BR-3, which strongly expresses HER-2; and A549, which weakly expresses this receptor. Plasmon resonance measurements showed that nanoparticles bound to the SK-BR-3 line showed a peak resonance that was significantly red-shifted compared to those bound to A549. This red shift, indicative of plasmon coupling, suggested the presence of receptor dimerization in the SK-BR-3 line. Refractive indices based on theoretical analysis using the Mie coated sphere model suggested that the scattering observed in the SK-BR-3 line can only be produced by receptor dimerization, an effect that was further confirmed by discrete dipole approximation models. The researchers suggest that this technique could prove useful for a variety of other cell and receptor types.