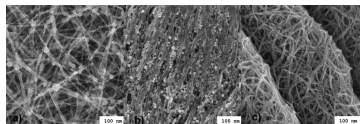


Road to Graphane Is Paved with Unzipped Nanotubes

■ The number of possible applications for single-walled carbon nanotubes (SWNTs) can be greatly expanded by modifying this material. For example, functionalizing nanotubes by attaching chemical groups or atoms or unzipping SWNTs into nanoribbons could lead to interesting and useful new materials. Currently, the most common method to unzip SWNTs is oxidation. However, this method also oxidizes the nanotubes, which could make them undesirable for some applications. A potentially better solution is hydrogenation, a method that could lead to the synthesis of



hydrogenated graphene (graphane) nanoribbons, a promising material for organic electronics.

To provide proof of concept, Talyzin *et al.* (DOI: 10.1021/nn201224k) subjected SWNTs to hydrogen gas at temperatures between 400 and 550 °C and pressures of 50 bar. Raman spectra of the nanotubes showed clear evidence of hydrogenation for those reacted at temperatures of 400–450 °C, a finding strengthened by valence band, infrared, and ultraviolet–visible spectroscopy. Such evidence was not apparent for those nanotubes reacted at temperatures higher than 450 °C, which showed significantly lower levels of hydrogenation on analysis by near-edge X-ray adsorption fine structure and X-ray

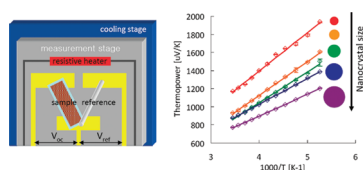
photoelectron spectroscopy. Further spectroscopic data suggested that hydrogenation could purify nanotubes from Fe catalyst particles by breaking down the fullerene-like coatings that surrounded these particles, leaving them vulnerable to acid treatment. Finally, transmission electron microscopy images provided evidence that those nanotubes hydrogenated throughout the entire temperature range had partially or completely unzipped, showing ends with balloon- or cone-like features or dimensions characteristic of nanoribbons. Taken together, these findings suggest that hydrogenation could be a viable way to create graphane nanoribbons from SWNTs.

Thermopower Lends Hot New Insight into Semiconductor Nanocrystal Solids

■ Semiconductors possess the useful ability to change electronic properties through varying the electric field, light, proportion of impurities, or temperature. Varying the size of nanocrystals in semiconductor solids constructed from these particles can also tailor electronic properties. In bulk and nanocrystal semiconductors, the gap between the Fermi energy (E_F) and the transport energy level (E_T) can provide insight into the system's electronic properties. Though nanocrystal solids are increasingly being incorporated into complex architectures that could eventually play key roles in applications ranging from transistors to solar cells, few studies have attempted to measure and to interpret E_F , which is critical to device optimization.

In an effort to understand E_F in semiconductor nanocrystal solids, Ko and Murray

(DOI: 10.1021/nn2007817) used temperature-dependent thermopower measurements in PbTe nanocrystal solids to determine the position of E_F with respect to E_T directly. After synthesizing a series of nanocrystals with sizes varying from 6.4 to 11.5 nm, verified with small-angle X-ray scattering and transmission electron microscopy data, the researchers deposited nanocrystals from five size ranges into thick films. Thermopower measurements on these films were each positive, suggesting



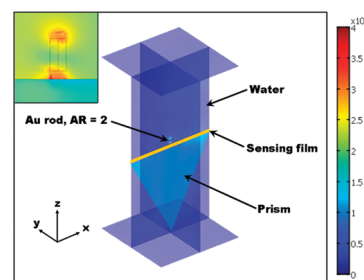
that holes are the main carriers responsible for electron conduction. Analysis showed that as the size of the nanocrystals was reduced, the gap between E_F and E_T increased, an effect the researchers attribute to the widening of the density of states (DOS) gap. Further investigation showed that narrowing the particles' size distribution sharpened the DOS, which in turn increased thermopower and conductivity. The authors suggest these findings provide new insight into how temperature affects charge carrier transport in semiconductor nanocrystal solids.

Improving Cancer Diagnostics by Enhancing Plasmon Resonance

■ Over the past decade, surface plasmon resonance (SPR) biosensors have gained more and more traction in pharmaceutical and biomedical research for studying various biomolecular interactions. These sensors operate by detecting small refractive index changes and passing along information about interactions between analytes and immobilized receptors on the metal surface through optical characteristics including intensity, phase, and polarization. These setups can detect interactions using analytes in the pM range. However, DNA, cytokines, and other small molecules are not detectable using this current paradigm.

Seeking to improve the sensitivity of existing SPR biosensors, Law *et al.* (DOI: 10.1021/nn2009485) created an enhanced biosensor by using gold nanorods as SPR signal enhancers. The researchers prepared gold sensing films lined with capture antibodies for tumor

necrosis factor alpha (TNF- α), a mediator of inflammatory and immune function that is also thought to initiate and to promote tumor growth present in only small quantities in human plasma. They then exposed the prepared films to TNF- α antigen to detect antibodies to which gold nanorods had been conjugated. Using a laser source whose wavelength matched the plasmonic resonance of the gold nanotags, the researchers found significant enhancement of the SPR signal. Tests using a range of TNF- α concentrations showed that the gold nanorods in this "sandwich" immunoassay led to up to 40-fold increases in sensitivity and the ability to detect the antigen at concentrations in the fM range. These findings suggest that gold nanorods could serve as promising amplifiers to improve existing SPR biosensor technology.

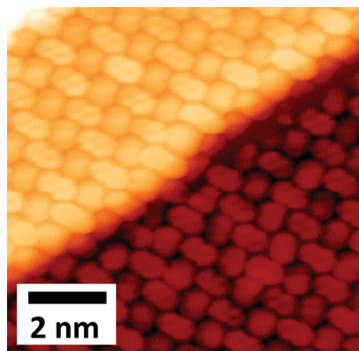


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Layering Gets More Fashionable on Epitaxial Graphene

■ Graphene has attracted increasing interest for use in nanoelectronics due to its unique electron-transport properties, including high carrier mobilities. For this material to serve as an integral part in field-effect transistors, it



must be layered with high-dielectric-constant films that are ultrathin, smooth, and defect-free to serve as gate insulators. However, because graphene is chemically inert and hydrophobic, dielectric layers grown or deposited on bare graphene substrates tend to be rough and nonuniform, leading to electrical performance that is less than desirable. In previous efforts to coat graphene with materials that might improve dielectric film deposition, materials including ozone, nitrogen dioxide, and polymers have been shown to damage graphene, and in turn, affect its electronic properties.

Seeking a better way to layer graphene with dielectric thin films, Alaboson *et al.* (DOI: 10.1021/nn201414d) looked to perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) as a coating material. After subliming

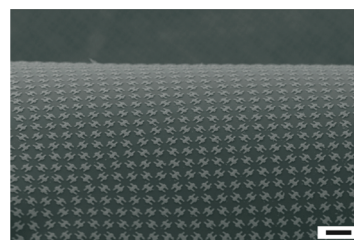
PTCDA onto graphene substrates under ultra-high vacuum conditions, scanning tunneling microscopy images showed that this material self-assembled into a homogeneous and well-ordered monolayer with a low-defect, herringbone structure. The researchers then stacked these modified graphene substrates with dielectric films composed of either HfO₂ or Al₂O₃. Further investigations showed that the resulting films were highly uniform with low defect densities and were securely attached to the substrate. High-resolution X-ray reflectivity measurements showed that the underlying graphene remained intact and undamaged. Capacitors constructed from these layered materials had high capacitance and low leakage currents. The authors suggest that PTCDA could eventually play a key role in preparing graphene for nanoelectronics.

Metamaterials Go to the Dark Side

■ In recent years, a number of efforts have been directed toward creating new optical metamaterials, materials engineered to have a tailored electric and magnetic response to specific wavelengths of light. Most metamaterials synthesized thus far have extremely low absorption loss, leading to applications including perfect lenses, flat collimating lenses, and invisibility cloaks. However, another less-studied class of metamaterials completely absorb incident light at wavelengths of interest. These metamaterial absorber (MMA) designs could have applications ranging from microwave-to-infrared signature control to thermal imaging. Some MMAs have already been engineered to absorb microwave and terahertz wavelengths. However, few operate in the infrared-to-visible range or absorb multiple bands.

To expand MMA capabilities, Jiang *et al.* (DOI: 10.1021/nn2004603) used a genetic algorithm (GA) to design nanoscale resonators with dual absorption bands in the mid-infrared range at 3.3 and 3.9 μm wavelengths. The GA, combined with a full-wave electromagnetic solver, resulted in an optimized design of gold H-shaped nanoresonators layered onto the flexible polymer Kapton, which in turn was layered on a thin gold film. Simulations suggested that absorption would be higher than 90% for an incident angle of up to 50° for both wavelengths; findings closely matched in laboratory performance after testing the reflectivity of the fabricated three-layer structure using Fourier transform infrared spectroscopy. The researchers performed further simulations of this material on a curved metal surface. Results showed that

reflection was nearly eliminated on a coated surface, in contrast to significant reflection on an uncoated surface. The authors suggest that this MMA design shows promise for advanced coatings for infrared absorption.



Harnessing Wasted Energy through Metamaterial Design

■ The extreme field confinement of plasmonics has lent itself to numerous applications, including bioimaging, biosensing, and photovoltaics. However, surface plasmons generally direct excitation to transverse magnetic (TM) polarized incidence, wasting transverse electric (TE) polarized incidence. Stepping beyond natural surface plasmons, some researchers have engineered designer plasmons, known as spoof plasmons, that can guide and focus light at various wavelengths. However, these spoof plasmons are also limited to transverse magnetic fields. Consequently, for unpolarized light, half the energy that could be used for plasmon excitation is wasted.

Seeking a way to harness TE polarized incidence, Feng *et al.* (DOI: 10.1021/nn201181p)

designed a textured metallic metamaterial that propagates surface plasmons with pure TE incident polarization, transverse to both surface plasmons and the plane of incidence.



The researchers engineered a plasmonic metamaterial constructed with Au stripes patterned in a deep subwavelength scale. Computer simulations showed that the thin metallic stripes prompted pure TE-to-plasmon coupling for visible wavelengths ranging from 540 to 680 nm. Calculations determined an optimal geometry for a focal wavelength of

640 nm with a period of 140 nm, slit width of 40 nm, and slab thickness of 55 nm. Using focused-ion-beam milling, the researchers fabricated this ideal plasmonic Au material on a glass substrate. This material demonstrated enhanced TE-to-plasmon coupling with close to 100% efficiency, a performance closely in line with simulated results and far above the efficiency of natural materials. The authors suggest that this design could translate into improving plasmonic excitation for numerous applications.

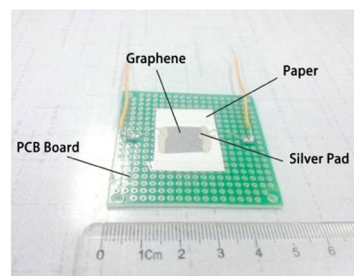
The Hills Are Alive, with the Sound of Graphene

Graphene's extraordinarily high mobility and thermal conductivity have made it a prime choice for a variety of applications, including graphene-based field-effect transistors, nonvolatile memory, photodetectors, and gas sensors. However, one potential field for which graphene has not been explored is acoustics.

In a new study, Tian *et al.* (DOI: 10.1021/n2009535) made the discovery that graphene can be used to generate sound. The researchers built sound-emitting devices by synthesizing multilayer sheets of graphene, then manually transferring these onto filter paper. Using stencil masks, they printed contacts onto the graphene-paper combination onto printed circuit boards, which supplied mechanical support and were used for es-

tablishing electrical connections. After setting up a test platform with a signal generator, a standard microphone, and a dynamic signal analyzer, the researchers supplied an electrical signal to the graphene through the silver contacts. They found that the device generated sound in frequencies ranging from 3 to 50 kHz. Analysis showed a flat frequency response in the 20 to 50 kHz range. Testing sheets of graphene that were 100, 60, or 20 nm thick, the researchers found that the thinnest sheets produced the highest sound pressure levels due to its lower heat capacity per unit area. Further investigation suggested that the graphene-based devices produced sound *via* the thermoacoustic effect, with electricity converted into joule heating by the graphene, generating sound pressure through changing air temperature. The

authors suggest that these findings can move graphene into acoustics, potentially leading to applications ranging from earphones to buzzers.



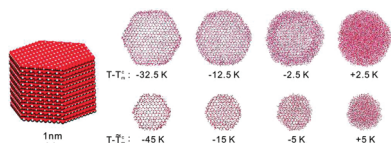
Ice, Ice Nano

Melting ice is an everyday event, yet on the nanoscale, this phenomenon remains relatively unexplored. A few studies have attempted to elucidate the particulars surrounding this phenomenon, for example, concentrating on nanoscale ice clusters melting on metal substrates, using computer simulations to explore melting of individual ice nanocrystals, or studying the melting of ice nanocolumns. However, questions remain, including how size might change melting

behavior, how morphology changes as nanocrystals melt, and where melting is initiated on nanocrystals. Answering these questions has practical implications for understanding noctilucent clouds, "night shining" clouds that contain ice nanocrystals and are thought to be connected to climate change.

To understand the melting behavior of ice nanocrystals, Pan *et al.* (DOI: 10.1021/n200252w) performed a series of molecular dynamics simulations with a TIP4P forcefield on hexagonal crystals from 2–8 nm in size, composed of 768–9600 water molecules. These simulations showed that melting temperature varied with size according to the Gibbs–Thomson relation, with smaller nanocrystals melting at lower temperatures

than larger ones. As crystals melted, they morphed from hexagonal to spherical shapes. Results showed that nanocrystals had pre-melting, a layer of quasi-liquid forming on crystal surfaces, at as low as 130 K below bulk melting temperatures, with the smallest nanocrystals developing premelting at the lowest temperatures. Further simulations showed that melting occurred first on the corners, where three edges meet, then on the edges, and last on the facets. The authors note that these findings add further insight into ice melting at the nanoscale, which could hold implications for environmental science.



Topological Insulator Conductivity Attacked by Air

Topological insulators (TI), unusual materials that act as insulators in their interiors while readily allowing charge transport on their surfaces, have excited considerable interest for both fundamental and applied studies. One such TI, layer-structured Bi_2Se_3 , behaves as an excellent example, with a single Dirac cone residing in a bandgap of about 300 meV. Several studies have revealed metallic surface states on Bi_2Se_3 . For example, transport experiments revealed Shubnikov-de Haas oscillations in the surface states in bulk and gated thin flakes of Bi_2Se_3 . However, some studies have shown that air can contribute to n-type doping in this material, degrading surface transport properties and making studies of surface states more difficult.

To elucidate how ambient conditions affect Bi_2Se_3 , Kong *et al.* (DOI: 10.1021/n200556h) undertook transportation measurements and surface composition analyses by X-ray photoelectron spectroscopy (XPS) on Bi_2Se_3 nanoribbons. Detailed transport studies using four-probe magnetoresistance and cyclotron effective mass analysis suggest the presence of excessive low-mobility carriers from environmental doping. To examine the source, the researchers probed the nanoribbons' and bulk surface crystals' surface chemistry with XPS. They found that as time in air increased, both nanoribbon and bulk Bi_2Se_3 showed proportionally rising concentrations of bismuth oxide. Over extended periods, the presence of selenium oxide was also observed. Bismuth oxide was

detected even on crystal samples whose freshly cleaved surfaces were exposed to air for only 10 s, evidence that oxidative degradation of this material happens very quickly. The authors suggest that Bi_2Se_3 may require careful handling to prevent surface degradation, such as encapsulation or surface passivation.

