

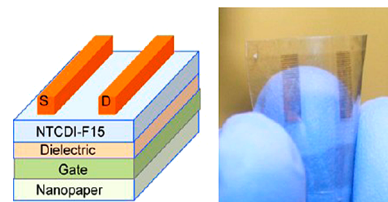
### A Transistor That Is One for the Nanopapers

Researchers are increasingly focusing on new types of macroelectronics made from green materials using roll-to-roll processes, characteristics that enable the development of inexpensive and disposable consumer electronics. Printable electronics are part of this new wave, with conductors, thin film transistors, organic light-emitting diodes, and solar cells already demonstrated in this regime. However, although previous efforts toward printable electronics have focused on developing new inks or fabrication processes, incorporating new nanomaterials, or devising new device structures, substrates have been comparatively underappreciated.

Helping to fill this gap, Huang *et al.* (DOI: 10.1021/nn304407r) crafted transistors

using a nanofibrillated cellulose base. This nanopaper is made of the same material as traditional paper, but its fibers have much smaller diameters. These smaller fibers decrease optical scattering, which increases optical transparency, resulting in flexible, transparent substrates that can replace plastic substrates in field-effect transistors (FETs). To test this substrate's utility in this role, the researchers fabricated a FET using a film of single-walled carbon nanotubes as the gate electrode, a poly(methyl methacrylate) dielectric layer, and a transparent semiconductor film. Evaluating their device's performance with electrical characterization, the researchers show that its mobility is comparable to other n-type organic FETs.

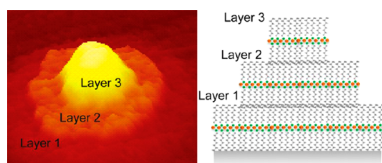
This mobility decreased only minimally when the device was bent either parallel or vertical to the conduction channel. The authors suggest that the excellent optical, mechanical, and electrical properties shown in this study demonstrate that nanopaper could have potential for next-generation electronics.



### Getting Inked in a New Way

Researchers have been using dip-pen nanolithography (DPN) since the early 2000s to pattern chemical adlayers on surfaces or to pattern "soft" materials, such as biological molecules. This technique involves using an atomic force microscope (AFM) tip coated with molecular inks to precisely deliver molecules to a substrate. Theoretically, DPN provides the ability to apply ink in a layer that is just one molecule thick. However, there is currently no way to control the precise number of layers in a deposited feature.

In a new study, Radha *et al.* (DOI: 10.1021/nn306013e) examine a novel liquid ink for DPN that is capable of forming layers in a controlled, sequential fashion. The



researchers relied on Pd alkanethiols as their prototypical ink. Using a dilute solution of Pd alkanethiol in toluene, the researchers used DPN to transfer layers of this ink to a Si substrate. Their experiments show that it is possible to control the number of layers deposited onto the substrate through the AFM tip's dwell time. Within 0.01 s, a single layer was deposited, with a second layer

deposited within 0.05 s, and a third layer by 0.1 s. The number of layers could also be controlled by ink concentration, with only monolayers being formed at 10 mM regardless of dwell time. Using this knowledge, the researchers were able to write features onto substrates, transferring some into metallic Pd by annealing and transforming others into nanocircuitry through electroless deposition of Cu. The authors suggest that this new ink represents an alternative to e-beam lithography for constructing metallic nanostructures.

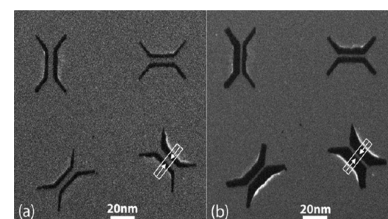
### Rust to Rust: Watching Carbon Nanotubes Oxidize

Oxidation can be both useful and detrimental. For example, controlled oxidation of silicon can produce gate oxides for field-effect transistors, but uncontrolled oxidation is responsible for the ubiquitous damage of corrosion in metals and alloys. Carbon nanotubes (CNTs), renowned for their electrical, thermal, and other useful properties, are not immune to corrosion. Shortly after their discovery, several groups attempted to use CNT corrosion to manipulate these properties, for example, by opening up their terminal caps or thinning the tubes. Although efforts were made to track these effects with transmission electron microscopy, because of the small sizes of the CNTs, researchers have yet to understand the underlying mechanism behind their oxidation.

In a new study, Koh *et al.* (DOI: 10.1021/nn305949h) offer new insights into CNT oxidation by observing individual CNTs in

an aberration-corrected environmental transmission electron microscope. Using multi-walled CNTs, the researchers tracked individual nanotubes in environmental gaseous cells as they were heated up to 520 °C while introducing oxygen. Whereas earlier reports suggested that CNT oxidation begins at the end of the tube and proceeds along the length, these new observations show that most often the outermost layer of the CNTs was removed first, while the nanotube cap remained at the end of the tube. On a few observed nanotubes, the interior wall was oxidized first, presumably due to oxygen entering through an open end or breaks in the tube. Carbon nanotubes with high numbers of walls, typically those grown by arc-discharge, were more resistant to oxidation. The authors suggest that these insights could provide new understanding of CNT oxidation, with the potential for better

manipulation or oxidation prevention for practical applications.



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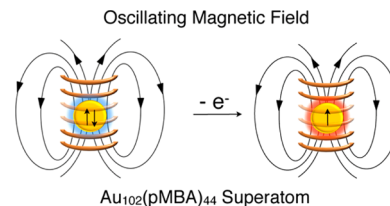
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### The Hot Attraction of Au Nanocluster Paramagnetism

■ Heating metal nanoparticles with an applied radio frequency (rf) field has been suggested for numerous applications, including hyperthermal therapy, biophysical manipulation, and enhanced catalysis, with Au nanoparticles being the best-studied examples. The mechanism behind this effect has been widely attributed to Joule-type heating, meaning that the nanoparticles behave much like small pieces of bulk metal. In this case, resistive heating would result from confined electrons forming eddy currents driven by electric fields surrounding the rf magnetic field flux direction. However, this mechanism has been disputed on both experimental and theoretical grounds. One possibility that has received little attention is the potential role that magnetic fields might play in heating.

Exploring this phenomenon, McCoy *et al.* (DOI: 10.1021/nn306015c) investigated heating in Au nanoclusters modified to become superatom paramagnets. Working with Au clusters modified with para-mercaptobenzoic acid (pMBA) ligands,  $Au_{102}(pMBA)_{44}$ , the researchers used  $KMnO_4$  to oxidize these nanoclusters chemically. Tests showed that  $Au_{102}(pMBA)_{44}$  behaved as a paramagnet after oxidation. By dissolving this material in water and exposing it to an oscillating magnetic field, the researchers show that the solution indeed increased in temperature. Successive oxidation attempts, which further increased the superatomic spin state of the clusters, increased the solution's initial heating rate. The researchers attribute this heating to the magnetic moment of the nanoparticle interacting with the oscillating

magnetic field. Calculations suggest that the mechanism is a combination of Brownian and Néel relaxations, much like the mechanism behind heating in magnetic iron oxides. The authors suggest that their findings add insight into the behavior of Au nanoparticles in rf fields.



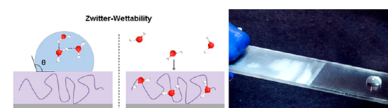
### Nixing Fog and Frost with "Zwitter-Wettability"

■ Antifogging and antifrost coatings that can handle a wide variety of environmental conditions have attracted increasing attention and research over the past decade. One potential way to address this challenge is through hydrophilic or superhydrophilic coatings that can reduce film-like condensation and thus light scattering. Although many of these developed coatings perform well in specific tests, none thus far can deliver acceptable light transmission in optical tests while avoiding image distortion across a range of aggressive fogging and frosting conditions.

Seeking a new way to address this issue, Lee *et al.* (DOI: 10.1021/nn3057966) developed a new type of antifogging coating that has the dual mechanism of rapidly absorbing

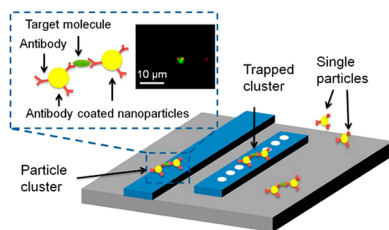
molecular water from the environment while also appearing hydrophobic when probed with water droplets. The researchers developed this novel coating by assembling multiple alternating layers of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). Tests show that a 30-layer film composed of these materials had a high level of frost formation followed by slow clearing to transparency, much like hydrophilic glass. To enhance antifrost behavior, the researchers modified the film with poly(ethylene glycol methyl ether) (PEG), which dispersed PEG molecules throughout the film, rather than just on the surface. This modification dramatically affected frosting behavior, rendering this new film frost-free throughout the experiment. The PEG-modified film provided

high transmission values and low image distortion, even under the most aggressive testing conditions. Further investigation showed that this film presents a highly hydrophobic character while also absorbing molecularly dispersed water. The authors suggest that this new film's characteristics could prove useful for antifogging and antifrosting under a variety of environmental conditions.



### Shedding Light on Plasmon Tunability

■ Better understanding of the collective electron oscillations known as plasmons has triggered a variety of applications, for example, in optical sensing, cancer therapy, and catalysis. Researchers have recently turned their attention to finding materials that can better control plasmonic performance with fast tunability. However, although they have found some success in materials such as superconductors in the sub-THz regime and conductive oxides in the visible and near-infrared, these materials have drawbacks, such as the need for cryogenic environments and/or demanding syntheses. Electrical tunability has also been suggested as a way to achieve these goals, but typical plasmonic materials such as Au and Ag have been shown to undergo only mild tuning despite massive charging.



In a new study, Fang *et al.* (DOI: 10.1021/nn3055835) demonstrate that plasmons can be controlled in graphene nanostructures through electrical doping as well as plasmon hybridization. Using graphene nanodisks sandwiched in a double-electrode configuration, the researchers show that both plasmon energy and strength increased with applied voltage, demonstrating plasmon tunability through electrical gating.

As the nanodisk size increased, so did the plasmon energy. Additional experiments with patterned nanorings resulted in plasmon hybridization that allowed operation down to light wavelengths of 3.7  $\mu m$ . The authors suggest that these two approaches can be readily extended to yield tunable plasmons in the near-infrared. By further tuning graphene plasmons, the authors suggest that these findings could translate into practical applications ranging from molecular sensing to communications and data processing.

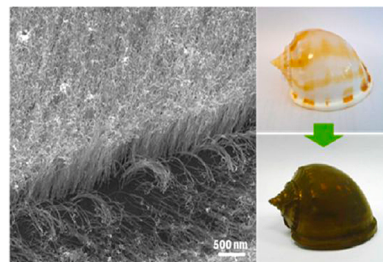
### Seeing the Au Nanowire Forest for the Trees

■ A variety of nanotechnology applications require controlling the conformation of nanocrystal growth. When nanocrystals are in solution, researchers have been able to steer their growth preferentially into certain shapes by exploiting facet-specific binding of surface ligands, consequently growing only certain facets. Nanowires are a special example of nanocrystals that have extremely large anisotropies. Typically, nanowires grown in solution have relied on weakly binding surface ligands, with mechanisms behind specific types of nanowire growth well-explained. Solution growth of nanowires anchored on substrates is more challenging.

In a new study, He *et al.* (DOI: 10.1021/nn4001885) report a new mechanism of nanowire growth that produces Au

nanowires grown from seeds on a substrate in polar solutions. The researchers started with adsorbed Au seeds on chips of Si wafer. Rather than exposing these seeds to weak ligands, as in solution-grown nanowires, the researchers instead relied on a strong ligand, 4-mercaptobenzoic acid (MBA). After submerging the seeded chips in a solution containing MBA,  $\text{HAuCl}_4$ , and the reducing agent L-ascorbic acid, scanning electron microscopy revealed a dense forest of Au nanowires growing from the chips' surfaces. Exposing only the seeds in solution produced only spherical nanocrystals, rather than nanowires. Further experiments suggest that the strong ligand inhibits growth everywhere on the Au nanocrystal seeds except at the substrate interface. There, Au can be continuously

deposited, causing the nanocrystals to grow upward from the substrate. The authors suggest that this mechanism can be used to create conductive surfaces, even with complex surface morphologies.



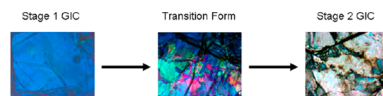
### Peeling Back the Layers of Graphite Intercalation Compounds

■ Graphite intercalation compounds (GICs) form when atomic, ionic, or molecular species intersperse between graphene layers in graphite. These stacks of doped graphene layers can be easily obtained in bulk quantities and have unique properties that are not present in the individual materials that compose them. The number of graphene layers sandwiched between two layers of intercalant is known as the stage number. How transitions between stages change the structure of GICs is not well-explained. Numerous models have been proposed, including the Daumas–Herold (DH) model, which suggests that islands of intercalant slide along graphene galleries to convert one stage into another. However, this and other models do not entirely

fit available experimental data, which consist mainly of macroscopic findings.

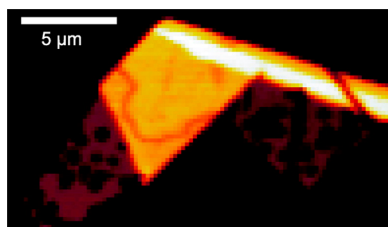
Taking a closer look at stage transitions, Dimiev *et al.* (DOI: 10.1021/nn400207e) monitored the microscale dynamics of these phenomena in real time using optical microscopy and Raman spectroscopy. As a model system, the researchers used the sulfuric acid GICs. The researchers created a stage 1 GIC by exposing graphite to a solution of ammonium persulfate in sulfuric acid. To induce deintercalation, moving from stage 1 to stage 2, the solution surrounding the graphite was diluted with water. The researchers' observations show that the stage transition began from the edges of graphite flakes, rather than the middle, as earlier studies suggested. As

deintercalation proceeded, a wave-like mechanical deformation swept across the flake surface, with intercalant entering and exiting graphite galleries independently of each other. The authors suggest that while these findings share features with the DH model, this theory does not encompass the complexity of the actual phenomena.



### A Brush with Greatness

■ Researchers in both academia and industry have become increasingly interested in block copolymers (BCPs) because of these materials' ability to self-assemble into periodic structures with domain spacing between 10 and 100 nm. The majority of BCPs synthesized thus far have domain sizes on the lower end of this scale, with potential applications in semiconductor industries. Although BCPs with large domain sizes have interesting potential as optical materials, synthesizing those that self-assemble with domains larger than 100 nm remains a challenge. One possible solution to extend the current size range is brush block copolymers (BrBCPs), compounds in which two or more different types of side chains are attached to a linear polymer in a block-wise manner.



To examine self-assembly in these compounds, Gu *et al.* (DOI: 10.1021/nn305867d) synthesized BrBCPs with polylactide and polystyrene side chains and polynorbornene backbones. Small-angle X-ray scattering and simulations revealed that these compounds self-assembled with domain spacings ranging between 20 and 240 nm. Domain sizes increased linearly with backbone length, suggesting that the

backbones stayed extended in the BrBCPs' ordered state. These BrBCPs appeared to assemble into well-ordered lamellae, with backbones perpendicular to the interface between lamellar domains. The quick timing of this assembly—under an hour—reflects a reduced number of entanglements between chains. The authors suggest that these BrBCPs provide an ideal way to study self-assembly of other BrBCPs and could potentially help inform the design of BCPs able to self-assemble into nanostructures with a greater range of domain spacing.