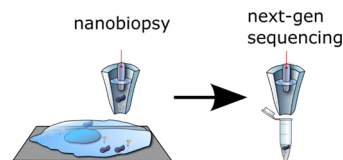


Giving Cells a Nanobiopsy

■ Taking tissue biopsies is an important part of diagnosing many diseases, particularly cancer. Even though it is well-known that cancerous tumors are heterogeneous and consist of cells at varying levels of transformation, tissue biopsies are only able to provide statistical averages of the many events happening among cells in the samples. Other anatomical tools used to study cellular heterogeneity and cell-to-cell interactions are usually employed post-mortem, limiting insight into cells' dynamic functions. While patch-clamp approaches that extract RNA have given some insight into the genomics of living cells, the micropipet used to impale cells effectively kills them, preventing analyses of changes in individual cellular genomics over time.

Looking for a way around these limitations, Actis *et al.* (DOI: 10.1021/nn405097u) developed a novel method to sample minute quantities of material from individual living cells, providing the ability to perform repeated genomic analyses. The researchers used an adapted scanning ion conductance microscopy method, a scanning probe technique in which a glass nanopipette is filled with an electrolyte solution and biased to generate ion flow through the aperture. If the nanopipette is immersed into an aqueous solution, such as that inside cells, applying a voltage across the interface can induce the aqueous solution to flow in or out of cells. Using this to their advantage, the researchers were able to sample mitochondria from individual cells

without harming them. Genomic analyses identified mutant mitochondrial genes using high-throughput sequencing. The authors suggest that these findings could set the stage for dynamic subcellular genomic analysis.



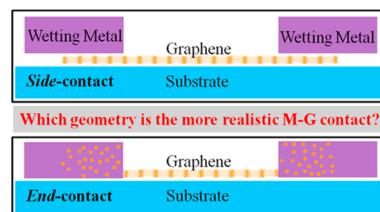
Side-Contact May Really Be End-Contact

■ The contact resistance of metal–graphene junctions continues to limit device applications. Metal electrodes such as Pt or Au that weakly interact with graphene, not forming chemical bonds or significant hybridization between the two surfaces, dope graphene in the contact regions, leading to n-i-n or p-i-p junctions throughout devices. This contact geometry, thus termed “side-contact”, assumes a metal slab on pristine graphene. Although this model is helpful for understanding electronic transport through graphene contacted by weakly interacting metals, it does not provide a realistic picture of interfaces with widely used “wetting” electrodes, including Pd, Ti, and Cr. Wetting electrodes have the potential not only to affect the electronic properties of graphene but also its structural properties,

forming a carbide. Thus, assumptions using the side-contact model may not provide a true impression of interfacial chemistry between wetting metals and graphene.

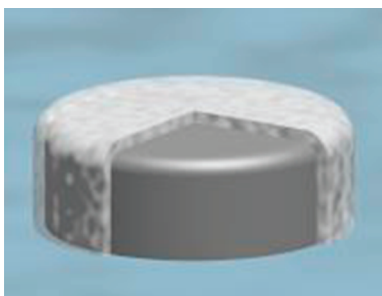
To investigate the interfacial behavior of wetting metals on graphene, Gong *et al.* (DOI: 10.1021/nn405249n) used *in situ* X-ray photoelectron spectroscopy to examine the bonding chemistry of Ti and Pd on as-synthesized graphene on Cu foil. After a single deposit of Ti, results suggested that Ti reacted with graphene to form a carbide, an example of end-contact geometry as opposed to side-contact. This finding was emphasized with subsequent applications of Ti, suggesting that at the interface Ti and C formed an alloy. Further experiments with Pd led to a similar conclusion. The authors assert that this work is consistent with

spontaneous formation of metal–graphene end-contacts during the metal deposition process as wetting metals react with graphene.



Popping the Top on Aluminum for Plasmonics

■ Plasmonics have the potential to revolutionize optics-based technologies at infrared and optical frequencies. However, while plasmons in nanoscale systems have been easily tunable across the visible and infrared regions of the spectrum, bringing plasmonic technologies into the UV has been more challenging because of inherent limitations in Au and Ag, the most commonly used plasmonic metals. Al has been suggested as an alternative plasmonic metal in the UV and visible regions of the spectrum and has numerous practical advantages, including low cost, high abundance, and ease of processing through a wide variety of methods. However, thus far, the optical response of Al has been inconsistent relative to theoretical calculations, preventing the application of Al to plasmonic devices.



Seeking the source of these inconsistencies, Knight *et al.* (DOI: 10.1021/nn405495q) measured the spectral response of Al nanodisks as a function of increasing disk diameter using a

custom-built hyperspectral UV–visible microscope. The nanodisks were crafted using three different deposition chamber conditions: pristine, recently “contaminated” with a thick layer of SiO_x, and cleaned following contamination with deposition of Ti as a getter and a sustained high vacuum for a week. Their results show that the plasmon resonance in the Al nanodisks

depended strongly on the presence of oxide within the metal, with the bulk plasmon frequency decreasing as trace SiO_x increased. This result was so reliable that plasmon resonances could be used as an optical reporter of the percentage of oxide present in Al. The authors suggest that these findings pave the way for Al to be used in low-cost plasmonic materials.

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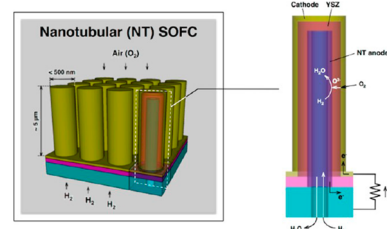
Powering Up with Nanotubular Arrays

■ Solid oxide fuel cells (SOFCs) efficiently convert energy stored in the chemical bonds of fuels directly into electrical energy. Compared to other types of fuel cells, SOFCs offer several advantages, including fuel flexibility, no concern about water management or methanol crossover, and the ability to use non-Pt catalysts. Using high aspect ratio one-dimensional (1D) nanostructures in SOFCs has potential advantages in terms of producing high surface areas. Recent studies have reported the use of electrodeposited metal nanowire arrays to increase the surface areas of electrodes significantly for other energy-conversion devices. However, thus far, researchers have not successfully integrated electrode–electrolyte–electrode assemblies into 1D fuel cells.

Seeking a novel way to improve the efficiency of SOFCs, Motoyama *et al.* (DOI:

10.1021/nn4042305) created SOFCs composed of nanotubular arrays of one-end-closed hollow tube Ni/yttria-stabilized zirconia/Pt membrane electrode assemblies (MEAs). The researchers synthesized nanotube MEA structures by sputter-depositing a Pt–Pd alloy film on a track-etched polycarbonate membrane. The film then served as a cathode for electrodepositing Ni nanowires into pores. After the membrane was removed, an ultrathin yttria-stabilized zirconia film was applied to the nanowires using atomic layer deposition, and the Ni was chemically etched away. To form a double-wall nanotube array, the researchers used core–shell Cu–Ni nanowires in the membrane, later removing Cu through anodic dissolution. Analyses of the novel SOFC's performance showed open circuit voltages of up to 660 mV and power densities up to $1.3 \mu\text{W}/\text{cm}^2$ measured at 550°C using H_2 as fuel. The authors

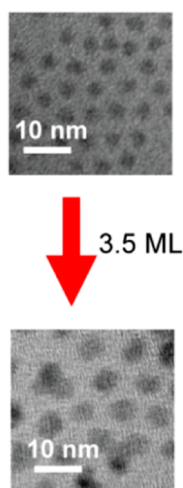
posit that the study is a significant step toward fabricating high-performance low-temperature SOFCs using the benefit of nanotube arrays to increase surface area.



Bright Future for Small, Charged Colloidal Quantum Dots

■ The Auger process occurs when the recombination energy of an electron–hole pair is transferred to another electron or hole (instead of a photon). Because it requires an activation energy, it does not significantly affect fluorescence in bulk wide band gap semiconductors because it is not efficient enough to compete with radiative recombination. However, in colloidal quantum dots (QDs), a fast Auger process leads to weak multiexciton emission and low brightness of trions, impediments to developing QD-based light-emitting applications. Strongly reduced biexciton emission rates have been achieved for CdSe/CdS nanocrystals, but only for those with thick shells. Such a design suggests that it may be impossible to develop small, bright, charged colloidal quantum dots.

In a new study, Qin *et al.* (DOI: 10.1021/nn403893b) suggest that negatively charged core/shell CdTe/CdSe QDs can fill this void. The researchers used electrochemical charge injection to introduce electrons into CdTe/CdSe QDs of different core sizes and shell thicknesses. They found that photoluminescent decay was significantly slower for samples with thin shells. Tests showed that the maximum ensemble



trion lifetime of ~ 4.5 ns was achieved with particles of ~ 4.5 nm diameter, the smallest particles with the brightest trion reported to date. Measurements in individual dots show that the negative charge suppresses blinking

and that the exciton can be as bright as the trion at room temperature. The authors note that these results improve understanding of multiexciton recombination in colloidal QDs and could lead to the use of small, bright, charged QDs for a variety of applications.

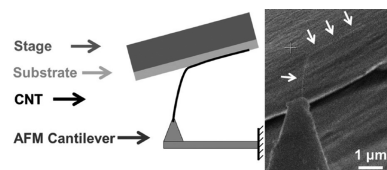
An A-Peeling Method for Quantifying Surface Energy

■ Carbon nanotubes (CNTs) continue to be one of the strongest, lightest materials yet developed. To increase their strength-to-weight ratio even higher, researchers have incorporated CNTs into macroscopic yarns and composite materials. At the nanoscale, the load in all CNT-based yarns is carried by tube–tube interactions through van der Waals forces between carbon atoms, noncovalent bonds between functional groups on the CNT surfaces, or covalent bonds brought about by cross-linking tubes. Even though individual CNTs are strong and stable due to bonding between carbon atoms, interactions between tubes are relatively weak, leading CNT yarns to have more inferior properties than would be expected based on their components. To improve

tube–tube interactions, researchers need to understand the interface between individual tubes.

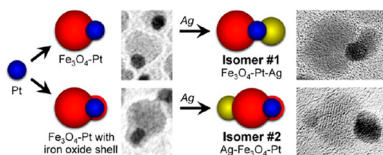
Toward this goal, Roenbeck *et al.* (DOI: 10.1021/nn402485n) investigated peeling of CNTs using experimental and computational methods. The researchers directly observed multiwalled CNTs being peeled off of a graphene substrate in a scanning electron microscope, measuring the force required with the deflection of a cantilever. They also used finite element and molecular mechanics simulations to analyze these data and to interpret their results. The researchers found that the surface energy at the tube–graphene interface is about 0.20 ± 0.09 or $0.36 \pm 0.16 \text{ J}/\text{m}^2$, depending on the tubes' conformation during peeling.

The authors suggest that these results might serve as a baseline for understanding the interactions between CNTs, and additionally, their experimental methods could be used to test functionalization that could improve the performance of carbon-based materials.



Protecting Groups Get Nanoparticle "Isomers" To Fall in Line

Colloidal hybrid nanoparticles are composed of several different nanoparticle domains in one system. They can exhibit properties unlike their constituent parts, a result of electronic and magnetic communication at solid-state heterojunctions within these assemblies. Their unique properties make them interesting candidates for a variety of applications, including solar cells, heterogeneous catalysis, magnetism, and electronics. The most common method for producing hybrid nanoparticles is a multistep seeded growth approach, in which preformed nanocrystals are used as seeds for sequentially adding more domains through subsequent reactions. Hybrid nanoparticles with the same components can be arranged in different linkages, in analogy to molecular isomers. However, the connectivity most likely to form in some systems is not the



desired conformation necessary for a particular application.

Seeking a new way to control domain arrangements, Hodges *et al.* (DOI: 10.1021/nn405943z) borrowed a strategy for directing reactivity to preferred functional groups in molecules: by installing a protecting group that prevents unwanted reactions from taking place. In a proof-of-concept study, the researchers show that it is possible to steer Ag to react with Fe_3O_4 in $\text{Pt}-\text{Fe}_3\text{O}_4$, rather than its

preferred target of Pt, by covering the Pt with a thin layer of iron oxide. They formed this protective layer by reducing the molar ratio of oleic acid to $\text{Fe}(\text{CO})_5$, two reaction precursors necessary to synthesize the hybrid nanoparticles. Various analyses confirm the presence of the protecting group, along with the desired formation. The protecting group on Pt also prevented reaction with Au, which reacts with Pt but not with Fe_3O_4 . The authors suggest that protecting groups might be expanded to other chemistries to improve the yields of desired configurations.

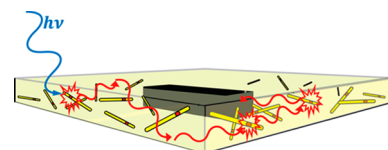
Bright, Sunny Day for Luminescent Solar Concentrators

Researchers have long sought to improve the efficiency of solar cells through the use of luminescent solar concentrators (LSCs). These adjuncts to photovoltaics typically consist of a luminescent dye, or lumophore, embedded in a polymer sheet that is attached to a high-performance solar cell. Sunlight gets absorbed in the lumophore, which luminesces into waveguides in the polymer sheet that in turn guide the light into the solar cell. A polymer sheet that is larger than the solar cell results in concentration of the solar photon flux. Luminescent solar concentrators operate by harnessing the Stokes shift of the lumophore. In the thermodynamic limit, the total energy lost to the Stokes shift is recovered as increased voltage from concentrated light on the solar cell.

However, results have been far less than this ideal due to excessive overlap between lumophore absorption and the emission spectrum. To approach the thermodynamic limit, a lumophore with a narrow emission spectrum and a large Stokes shift is necessary.

Toward this goal, Bronstein *et al.* (DOI: 10.1021/nn404418h) investigated CdSe/CdS seeded nanorods as a tunable lumophore in LSCs. By creating nanorods with a relatively large CdS rod and small luminescent CdSe seed, the researchers found that reabsorption of propagating photons was significantly reduced. Monte Carlo ray tracing simulations support these conclusions, suggesting that larger nanorods outperform smaller ones despite the larger nanorods' lower luminescent

quantum yields. The authors suggest that LSCs can be further improved by using particles with band gaps better matched to the solar spectrum, optimization of the LSC geometry, and photovoltaic cells better matched to lumophore emission.



Insights into Plates on Pores

Solid-state nanopores have potential in applications including sequencing, biosensing, and biophysics. Despite progress in this field, biological nanopores still offer several advantages over synthetic ones, including higher signal-to-noise ratios, slower DNA translocation velocities, and the ability to introduce new functionality by creating mutant proteins. By inserting biological structures into solid-state nanopores, some researchers are hoping to capture the advantages of both systems. One possibility is inserting DNA origami structures, created by building shapes from DNA held in place by oligonucleotide "staples", into solid-state nanopores. This technique can be used to design custom apertures made from DNA origami that fit over synthetic nanopores, enabling greater control of the nanopores' geometry and functionality.

Seeking more information about the structural properties of DNA origami in solid-state nanopores, Plesa *et al.* (DOI: 10.1021/nn405045x) studied DNA origami nanoplates docked on SiN nanopores. To simplify the system, their nanoplates had no apertures. The researchers studied several different nanoplate designs, including a honeycomb lattice, a Rothemund rectangle, and two- and three-layer lattices. Tests showed that each of these designs had high ionic permeability. The conductance of these nanoplates, compared to the bare nanopore, increased as a function of pore diameter and upon lowering the ionic strength of the surrounding solution. Results showed that the honeycomb lattice had the best performance, with the Rothemund rectangle second among the series. Surprisingly, the researchers found that, as voltage increased,

the nanoplates could buckle and even be pulled through the pore with sufficient force. The authors suggest that these findings can help researchers rationally combine DNA origami nanoplates into future nanopore designs.

