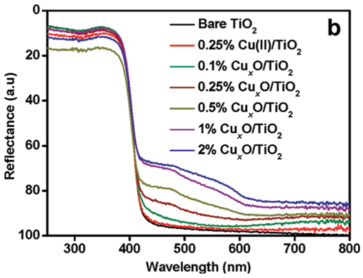
Shining a New Light on Indoor Risk Reduction

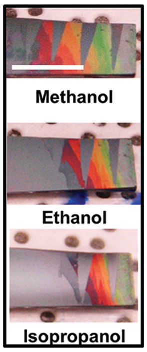
Volatile organic compounds (VOCs) and pathogens, including infectious bacteria and viruses, can both create poor indoor air quality, harming human health. For environmental remediation of these components outdoors, previous research has shown that the photocatalyst TiO_2 can be effective when used as a coating. However, this molecule is only activated by intense ultraviolet light, disqualifying it for indoor use. To sensitize TiO_2 for indoor light, some researchers have tried doping this photocatalyst with transition metal ions or with anions. However, the resulting materials have shown low light-harvesting efficiency and poor performance.

Seeking a novel material that both neutralizes VOCs and provides antipathogenic activity, Qiu *et al.* (DOI: 10.1021/nn2045888) combined TiO_2 with Cu^I and Cu^{II} species because previous work has indicated that Cu^{II} can oxidize VOCs and Cu^I has antibacterial and antiviral properties. The researchers grafted nanoclusters containing Cu^I and Cu^{II} onto TiO_2 particles in powders, confirming their presence with spectroscopic, microscopic, and other techniques. They then evaluated the effectiveness of their samples in eliminating VOCs and pathogens under visible light illumination characteristic of indoor environments. Their findings show that after exposure times of 96 h, the combined material eliminated a model VOC completely, unlike bare TiO_2 or TiO_2 doped with nitrogen. Similarly, the TiO_2/Cu nanocluster combination, coated onto glass substrates, was highly effective at killing bacteria and viruses. This last ability was present not only under visible light but also under dark conditions. The researchers suggest that these hybrid nanocomposites could be useful for a wide range of air purification applications.



Color Me Novel

Structural color relies on the physical properties of a material, such as its shape and density, rather than the chemical properties of pigments. This quality has attracted increasing attention from the research world since by these means materials are highly tunable, opening the possibility for easy-to-read, self-reporting sensors that go beyond the current array of commercially available colorimetric diagnostic tests. Because structural color does not rely on chemical state, sensors based on this factor would not need to rely on the chemical properties of a given system. Any new diagnostic based on structural color would need to be able to encode multiple responses from a single material, be highly sensitive to some general property for a class of materials, and produce a colorimetric response that is easy to read.

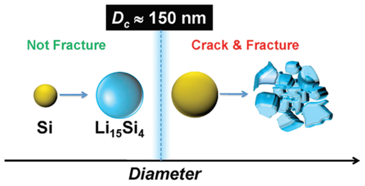


In a proof-of-principle study, Burgess *et al.* (DOI: 10.1021/nn204220c) produced a novel colorimetric sensor that meets each of these requirements. They base their novel wetting-in-color-kit (WICK) on defect-free silica inverse opal films (IOFs), a material that is well recognized to produce iridescent structural color. Relying on the minute differences in wetting between different liquids, the researchers developed IOFs that were chemically modified using a combination of two different alkylchlorosilanes to allow different amounts of liquid into pores. This technique provided colorimetric discrimination between various concentrations of ethanol, ranging from 85 to 100%. Taking this technique a step further, they exposed the modified IOFs to short bursts of oxygen plasma, affecting how pores filled. This allowed further discrimination of various other alcohols and alkanes. The authors suggest that WICK could have applications ranging from detection of forgeries to in-field identification of liquids.

What Makes Lithiated Silicon Nanoparticles Crack

Lithium batteries are already being used in a variety of small consumer electronics. To move these batteries into more demanding applications, such as electric cars, researchers will need to improve energy density and power capability radically. One material considered to be a promising anode candidate is silicon, which has a Li storage capacity about 10 times higher than that of carbonaceous anodes. However, Si expands to nearly three times its volume when alloying with Li, resulting in pulverization and loss of electrical contact, which leads to fading capacity with Si-based electrodes. Nanostructured Si-based electrodes somewhat mitigate these effects. However, thus far, researchers have not known the critical size above which lithiated Si nanoparticles break apart.

To answer this question, Liu *et al.* (DOI: 10.1021/nn204476h) lithiated individual spherical Si nanoparticles inside a transmission electron microscope to examine their behavior closely. Findings showed that during electrochemical or constraint-free chemical lithiation, nanoparticles above about 150 nm in diameter developed cracks and eventually fractured into multiple pieces when their Li_xSi shell reached the same thickness. Si nanoparticles smaller than this diameter did not crack or fracture, even though they underwent a nearly 300% volume expansion. The researchers suggest a mechanism in which a large buildup of tensile hoop stress reversed initial compression of the surface layer, resulting from movement of a two-phase boundary between the inner Si core and the outer Li–Si coating. Stored strain energy between the core and shell were not enough to drive fracturing in the smaller nanoparticles. The authors suggest these findings could help build more reliable and more stable Li batteries with Si anodes.

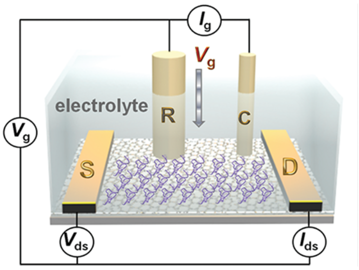


10.1021/nn300538m

Flexibility in Detecting Cancer Biomarkers

Single-atom-thick sheets of carbon known as graphene continue to draw enormous attention due to their excellent electrical, optical, and mechanical properties. Since native graphene lacks a band gap, researchers often dope this material with foreign atoms, tailoring its semiconducting properties and making it suitable for field-effect transistors (FETs). Graphene FETs have been suggested for a wide variety of applications. However, thus far, they have not formed the basis for flexible sensors to detect cancer biomarkers, a potentially useful and novel way of diagnosing, staging, and monitoring cancers.

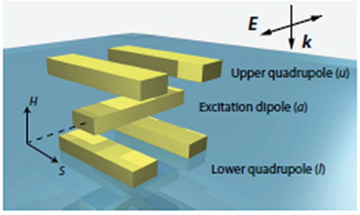
Moving graphene FETs into this realm, Kwon *et al.* (DOI: 10.1021/nn204395n) developed sensors that detect vascular endothelial growth factor (VEGF), an important cancer biomarker, by integrating an anti-VEGF RNA aptamer with doped graphene that uses conducting polymers with heteroatoms in their structure as the carbon source. The researchers grew polypyrrole-converted nitrogen-doped graphene on Cu foils using a combination of chemical vapor deposition and vapor deposition polymerization. They then transferred these few-layer graphene pieces onto flexible and transparent poly(ethylene naphthalate) film. After immobilizing the anti-VEGF aptamer onto these constructs, then assembling them between source and drain electrodes, the researchers show that the resulting FET is capable of detecting various concentrations of VEGF with response times of less than 1 s. The minimum detectable level was about 100 fM, up to 3 orders of magnitude lower than that of conventional VEGF sensors. Further tests showed that this sensor was reusable and had excellent flexibility. The authors suggest that this approach could be used in a wide range of biomedical and environmental applications.



How 3D Plasmonic Rulers Measure Up?

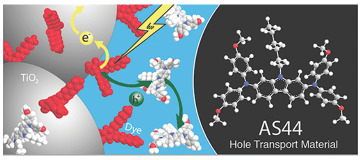
Localized surface plasmons—charge oscillations on the surface of metallic nanoparticles—can interact when nanoparticles are in close proximity, leading to optical resonances that depend on the distance between the nanoparticles. Consequently, this plasmonic interaction, and the resulting changes in optical spectra, can shed light on the distance between two nanoparticles. Based on this principle, researchers have constructed three-dimensional "plasmonic rulers" using two pairs of nanorods with a central dipole nanorod antenna in between—a useful tool for understanding biomolecules. However, questions of whether such a ruler can uniquely encode both the horizontal and vertical displacements of the central nanorod, as well as whether the ruler can be calibrated so displacements can be accurately measured have remained unanswered.

To address both questions, Davis *et al.* (DOI: 10.1021/nn204029p) used an electrostatic method to develop an analytical model of a three-dimensional plasmonic ruler. Using a series of calculations, the researchers identify the central nanorod's resonance as the key factor in the optical spectrum that encodes both horizontal and vertical displacement, which separately affect resonance frequency and strength. Based on this mathematical model, they show that it is possible to design the ruler so that the linear combinations of the nanorod coupling coefficients rely on just one of these displacements, allowing each to be uniquely measured. Further calculations linked the coupling coefficients to displacements of the central nanorod, allowing changes in its position to be measured if its initial position is known. The authors suggest that these findings will allow better ways to use plasmonic rulers in a variety of complex biological systems.



Filling a Need for Better Solid-State Dye-Sensitized Solar Cells

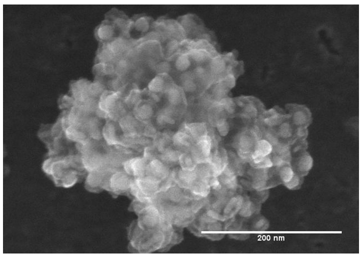
Dye-sensitized solar cells produce renewable energy using devices with substantially lower costs than conventional solar cells. These devices absorb incoming light with a sensitizing dye that, upon excitation, injects electrons into the conduction band of a titania network. The dye then regenerates, followed by hole transport to the solar cell's electrode. Most current devices use an iodide/triiodide redox couple to regenerate the dye and provide a mechanism for hole transport. However, this liquid electrolyte is corrosive and volatile, and the overpotential required for dye generation limits the maximum obtainable voltage. Recently, researchers have sought to overcome these problems using solid-state dye-sensitized solar cells (ssDSSCs) that take advantage of solid-state hole transport materials (HTMs). Thus far, the best-performing HTM is 2,2′,7,-7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD). However, its performance has been limited in thicker devices because it only partially fills their pores.



Seeking a better HTM for thicker ssDSSCs, Leijtens *et al.* (DOI: 10.1021/nn204296b) developed two new materials based on different chemical modifications of spiro-OMeTAD. Tests show that both materials have higher solubility than their precursor, along with low glass transition temperatures and low melting points—all qualities that could increase pore filling. p-Doped versions of both materials, known as AS37 and AS44, have mobilities similar to spiro-OMeTAD, and AS44 has higher conductivity. Tests show that thin devices made with these new HTMs rival the performance of ssDSSCs based on spiro-OMeTAD, and thick devices made with AS44 surpass spiro-OMeTAD ssDSSCs' efficiencies. The authors suggest that a melt infiltration process that increasingly fills pores might further boost efficiencies in thicker devices.

Nanoclusters Make Proteins Concentrate

Simulations and theory have suggested that high concentrations of a single type of protein, up to hundreds of mg/mL, can exist stably in solution in a compact, folded state. However, these ultrahigh concentrations have never been realized experimentally. Proteins' short-range attractive interactions tend to cause concentrated protein solutions to gel at substantially lower concentrations.



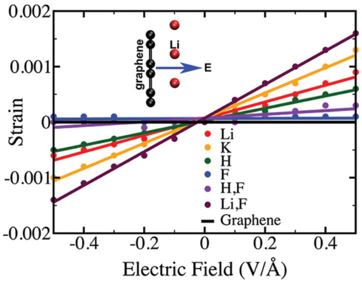
At fewer than 200 mg/mL, many proteins in solution aggregate irreversibly, gel, and precipitate out of solution. Such behavior represents a substantial barrier to applications in therapeutic delivery, limiting the storage and self-delivery potential of protein-based drugs, including those for cancer and many other diseases.

In a new study, Johnson *et al.* (DOI: 10.1021/nn204166z) demonstrate a novel solution to this problem by balancing attractive and repulsive interactions to form large clusters of proteins that stay dispersed in solution. Working with three types of model proteins, monoclonal antibody (mAb) 1B7, polyclonal sheep immunoglobulin (IgG), and bovine serum albumin (BSA), the researchers mixed lyophilized powders of single proteins with buffer and trehalose, a cosolute that increases short-range attraction between protein molecules through a crowding mechanism. Choosing a buffer concentration with a pH near the electrostatic point weakened electrostatic repulsion. The result was protein clusters about 100 nm in diameter that remained separate at concentrations of several hundred mg/mL in solution. Upon dilution, these nanoclusters dissociated into monomers, shown with various biophysical analysis techniques. *In vivo* experiments in mice showed that the nanocluster protein solutions had identical pharmacokinetics as the same proteins in standard solution. The authors suggest that such nanocluster protein solutions could have numerous applications for biological therapeutics.

Graphene Feels the Strain

Graphene's unusual and useful optical, electronic, and mechanical properties have made it a favorite for developing a variety of new technologies, including field-effect transistors, detectors that can sense gases at the single-molecule level, and new generations of solar cells. Numerous theoretical works have suggested that controlling and engineering strain could lead to even more novel devices in which mechanical deformations could control optical or electronic properties, a field dubbed straintronics. However, piezoelectricity has traditionally been thought to be an intrinsic property of materials with wurtzite or related structures. Consequently, graphene has not been considered piezoelectric.

Turning this paradigm around, Ong and Reed (DOI: 10.1021/nn204198g) show in a new study that it is possible to engineer piezoelectric graphene by selectively adsorbing atoms onto its surface, thereby breaking graphene's inversion symmetry. Using density functional theory and Li, K, H, and F as models, the researchers show that doping with adatoms changes the electromechanical properties of pure graphene. Calculations show that uniform coverage of F on graphene, or H and F on opposite sides, results in only a small change to the strain piezoelectric coefficient. Bound Li or K resulted in moderate changes in this coefficient. Asymmetrically adding F over carbon atoms on one side and Li or K in hollow sites on the other side of graphene changed the piezoelectric coefficients by the highest values. As expected, a higher coverage increased piezoelectricity more than lower coverages. These results suggest that piezoelectricity can be engineered into graphene, an effect that could lead to the development of new types of nanoscale electromechanical devices.



Shining a New Light on SERS and Luminescence

Much remains unknown about how various factors influence surface-enhanced Raman scattering (SERS), such as how a nanoparticle's shape, size, and degree of aggregation influence this phenomenon. Understanding the effects of these factors, especially how they affect the electromagnetic field enhancement in nanoparticle junctions, are pivotal to designing effective SERS substrates. In previous research, Weber *et al.* located and tracked the origin of the SERS signal from the fluorescent dye molecule Rhodamine 6G attached to NaCl-aggregated silver nanoparticle colloids. Even when no SERS signal was observed, the researchers still found a weak silver photoluminescence background signal. Multiple experiments showed that sometimes the strongest SERS emission was located within the luminescence, but other times, the two signals were separated by tens of nanometers. Although the aggregate's structure is a likely source for the signals' offset, structural analysis using scanning electron microscopy was not able to clarify the source.

In a new study, Weber *et al.* (DOI: 10.1021/nn205080q) examined silver nanoparticle colloids that were aggregated with NaBr, which improved citrate displacement and eliminated the citrate spectral signal. Superresolution optical imaging, down to the sub-5 nm level, showed that SERS and luminescence emanated from different locations on the nanoparticle surface. Correlated scanning microscopy revealed that both signals were plasmon mediated. However, the SERS signal is highly local, originating from a single junction in an aggregate, while the luminescence originates from all plasmon modes in the nanostructure. Discrete-dipole approximation calculations supported these findings. The authors suggest that these findings, which better explain SERS emission in aggregates, can help in developing new theoretical models of SERS phenomena.