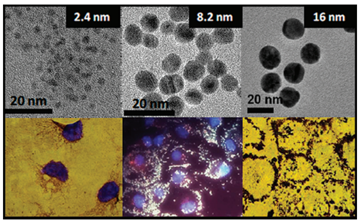
How Cells Go for the Gold

Recently, gold nanoparticles (AuNPs) have attracted increasing interest from the biomedical community for applications including imaging, diagnostics, and therapy. Each of these uses relies on controlled cellular uptake and directed delivery to the cytosol or various organelles. To reach this goal, some researchers have engineered functionalized coatings for the outer surface of AuNPs that make these materials more hydrophilic and biocompatible, with targeting molecules that encourage cells to take in AuNPs and deliver them to the desired destinations. However, size, surface coatings, and further biofunctionalization can interact in complex ways, each significantly affecting cellular uptake and distribution.

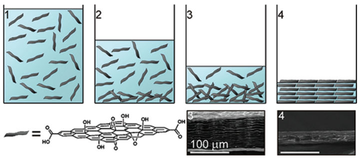
To get a better understanding of how each modification changes uptake and delivery, Oh *et al.* (DOI: 10.1021/nn201624c) synthesized AuNPs with diameters ranging from 2.4 to 89 nm. They coated each batch of nanoparticles with poly(ethylene glycol)-functionalized dithiolane ligands that terminated in either carboxyl or methoxy groups. To those terminating in carboxyl groups, the researchers covalently attached a cell-penetrating peptide (CPP) derived from the human immunodeficiency virus. After characterizing the AuNPs using various methods, the researchers exposed COS-1 cells to these nanoparticles. A combination of methods showed that only cells modified with the CPP were endocytosed. AuNP diameter ultimately determined intracellular destination, with the smallest nanoparticles being delivered to the nucleus and intermediate nanoparticles delivered to the cytosol. Nanoparticles that were 16 nm or larger did not enter cells. The authors suggest that these findings emphasize the need to explore how other factors, such as cell lines, exposure times, and different surface ligands, can affect nanoparticle fates in cells.



Graphene Oxide Paper Assembly: Order or Chaos?

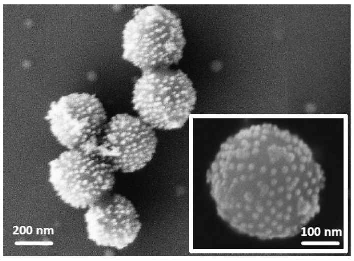
Thin papers made of individual graphene-based nanosheets layered into brick-and-mortar formations have been shown to have exceptional strength, while retaining great flexibility and ductility. Although their mechanical properties have been well explored, their formation mechanism remains unclear. These papers are typically fabricated through the flow-directed filtration of a fluid containing dispersed nanosheets onto a supporting membrane. Their formation is likely to entail one of three mechanisms: either highly ordered layers, in which the nanosheets lay down sequentially; a disordered concentration, in which the nanosheets remain in disarray until geometric confinement pulls them into their final ordered arrangement; or semi-ordered accumulation, an intermediate between the other alternatives.

To determine which possibility is most likely, Putz *et al.* (DOI: 10.1021/nn202040c) performed a series of experiments using thermal gravimetric analysis, UV–vis spectroscopy, and X-ray diffraction on nanosheets in solvent during filtration. Results showed that nanosheet concentration during filtration remained relatively stable and effluent volume did not show a linear trend, ruling out the disordered concentration paradigm. Similarly, adding polymer chains of various lengths to the liquid during filtration showed that longer chains could snake through the nanosheets, ruling out the highly ordered paradigm. Experiments using powder X-ray diffraction on drying water-soaked samples of graphene oxide paper confirmed that the semi-ordered accumulation is probably the correct mechanism. The authors note that these findings not only add new knowledge to graphene oxide paper formation but also suggest new ways to design customized nanocomposite papers with added nanoparticles or molecules of different sizes and shapes.



Attractive Idea: Core–Shell Clusters with a Magnetic Dipole Response

Metallic nanoparticles, and composites made of these materials, have been the focus of numerous investigations over the past century, mostly due to their intriguing localized surface plasmon polaritons that can be excited at discrete wavelengths. These unusual excitations, carrying energy partly in a photonic state and partly in a plasmonic state, arise from the interface between a metal and a dielectric, allowing external electromagnetic waves to drive charge-density oscillations in the metal. Most of the applications that exploit these properties, including biosensors or hyperthermal therapy for cancer, rely on resonances with an electric dipolar character. However, these materials' magnetic dipolar responses are pivotal for other applications, such as those in optics or imaging. Though several top-down and bottom-up strategies have been employed to fabricate nanoparticle composites with a strong magnetic response, they suffer from limitations that make their use in future applications unlikely.



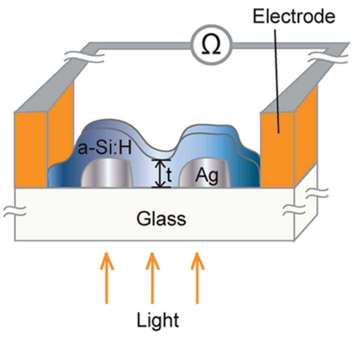
Seeking a new way to create these materials, Mühlig *et al.* (DOI: 10.1021/nn201969h) used two distinct self-assembly processes to create core–shell clusters with a strong, isotropic magnetic response in the visible spectral domain. The first process used electrostatic forces to surround positively charged silica nanospheres, about 78 nm in diameter, with negatively charged gold nanospheres, about 8 nm in diameter. The second process used thiol chemistry to attach 10 nm gold spheres to 130 nm silica ones. Theoretical analysis and experimental characterization showed that the extinction spectra of both assemblies were dominated by a resonant magnetic dipole moment. The authors suggest that both of these assemblies represent unique structures with an artificial magnetic response that could prove useful in a variety of future applications.

10.1021/nn202927z

Thin Is in for Hydrogenated Amorphous Silicon Solar Cells

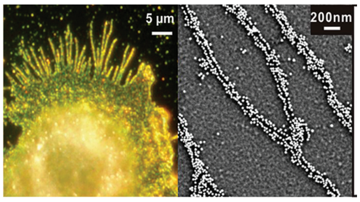
Hydrogenated amorphous silicon (a:Si-H) solar cells have thus far shown experimental conversion efficiencies of about 10%, far below the theoretical limit of 27%. This difference results mostly from high-density tail and defect states in the a:Si-H band gap, which significantly lower performance. To get around this problem, such solar cells are often constructed with p- and n-doped layers sandwiched around a light-absorbing layer. Generally, thicker layers maximize optical absorption, and thinner layers minimize recombination and transport losses. Recent studies suggest that combining a:Si-H with nanoparticle plasmons can improve the design of these devices, allowing smaller losses of optical absorption with thinner layers. However, exactly how a:Si-H layer thickness contributes to these processes has been unknown.

To investigate this question, Gusak *et al.* (DOI: 10.1021/nn201074z) laid a:Si-H films of varying thickness ranging from 9 to 67 nm over Ag nanodisks on a glass substrate. They analyzed these systems using both optical spectroscopy and photoconductivity. Results showed that the plasmon resonance of the nanodisks shifts with the a:Si-H thickness, starting at about 480 nm for bare Ag nanodisks on glass to about 600 nm for those covered with a 12 nm film and 680 nm for those covered with a 32 nm film. For the thickest films, a quadrupolar plasmon resonance mode becomes visible. The experimental data, along with finite element calculations, suggest that total absorption associated with the dipolar mode reaches its maximum in very thin a:Si-H films and decreases with increasing thickness. The authors suggest that these results support the development of ultrathin "two-dimensional" plasmonic solar cells to bring efficiencies closer to the theoretical maximum.



Shining a New Light on Receptor Densities

Filopodia, spike-like projections on bundled actin extensions called lamellipodia, help cells migrate throughout the body. Such motility is important for normal growth and healing, such as closing wounds, as well as for causing pathological states, such as cancer metastasis. Besides assisting generation of a motile force, filopodia are also thought to have a diverse array of additional biological functions, including serving as biological antennae that sense molecules such as growth factors for chemotaxis. If filopodia indeed have this function, some researchers have suggested that they may display a proportionally higher density of receptors for these molecules. However, studies have not yet mapped the spatial distribution of receptors on filopodia to support this theory.

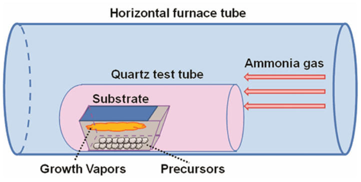


Seeking a reliable way to determine the density of key molecular receptors on filopodia, Wang *et al.* (DOI: 10.1021/nn202055b) developed a novel method that combines electron microscopy and optical plasmon coupling microscopy. The researchers used a multistep method to tag the epidermal growth factor receptor, a cell-surface receptor thought to be overexpressed in a variety of different cancers, with Au nanoparticle immunolabels. Resonance wavelengths showed that the filopodia displayed higher densities of Au nanoparticles compared to the cell membrane. Scanning electron microscopy confirmed these findings, showing nanoparticles preferentially clustering on the filopodia's long axes. Quantifying the relationship between resonance wavelength and SEM characterization generated a model that the researchers used to determine nanoparticle density by spectral response, generated by near-field interactions between nanoparticle neighbors. The authors suggest this method could be extended to determine the density of other receptors important for biomedical applications.

Succeeding at Drying with Anti-wetting BN Nanosheet Coatings

Single- or multilayer carbon nanosheets have attracted an increasing focus on two-dimensional (2D) structures in recent years due to their potential in numerous applications, including biosensing, gas detection, and electron emission. Likewise, structurally similar 2D boron nitride (BN) nanosheets have unique properties, such as excellent thermal conductivity, mechanical strength, and electrical conductivity. Additionally, nanostructured BN films have shown superb hydrophobicity, suggesting potential applications in water repelling, antifouling, and self-cleaning coatings. Developing a simple and efficient approach to creating customizable BN films, with varying levels of hydrophobicity, would be of enormous interest for these new technologies.

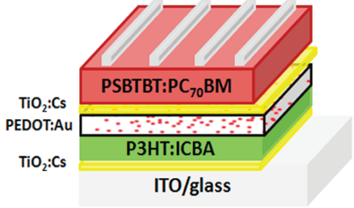
In a new study, Pakdel *et al.* (DOI: 10.1021/nn201838w) detail such a method they developed to create BN nanosheets on Si/SiO_2 substrates. Using B, MgO, and FeO powders as precursors and NH_3 gas flow in a conventional horizontal tube furnace, the researchers created films composed of individual BN nanosheets on substrates. Experiments showed that the morphology, and resulting characteristics, of the finished coatings strongly depended on the growth time and temperature. Fine and closely distributed nanosheets formed at temperatures as low as 900 °C and growth times as short as 30 min. However, as temperatures and growth times increased, larger nanosheets formed and spacing increased. These larger nanosheets showed bent and scrolling conformations, increasing surface roughness. Tests showed that contact angles on those coatings formed at the highest temperatures, 1200 °C, had contact angles greater than 159°. The authors suggest that BN nanosheets synthesized in this way could eventually have numerous industrial applications.



Bridging the Gap: Au Nanoparticles in Tandem Solar Cells

Polymer-based organic solar cells hold promise for renewable energy, with organic bulk heterojunction cells currently showing power conversion efficiencies of 7%. However, quantum efficiency remains limited by relatively low carrier mobility, which is highly dependent on the thickness of the solar cell's active layer. A thin active layer enhances quantum efficiency, but a minimum thickness is necessary for light absorption. To achieve thinner active layers but optimize light harvesting, some recent studies have shown success in introducing metallic nanostructures into the active layer for generating plasmonic effects in single bulk heterojunction solar cells. However, researchers have not yet demonstrated the same advance in polymer tandem solar cells.

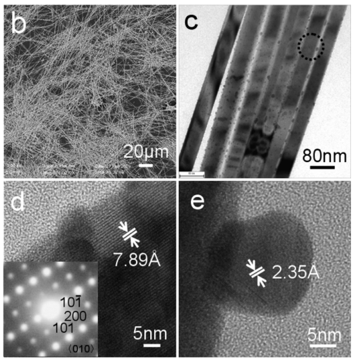
In a new study, Yang *et al.* (DOI: 10.1021/nn202144b) achieve this feat by incorporating Au nanoparticles into the interconnecting layer (ICL) joining the front and rear subcells of a polymer tandem solar cell. The researchers blended the nanoparticles into poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), a material used as a buffer layer in polymer solar cells. Tests showed that the incorporated nanoparticles did not change this material's transmittance, thickness, or electrical conductivity. However, devices containing the nanoparticles showed a boost in power conversion efficiency by about 20%, mainly due to a higher short current density. Further investigation suggests that this enhancement is due to higher absorption from the Au nanoparticles' plasmonic effects, which affect the performance of both cells simultaneously. Raman scattering experiments indicate that the nanoparticles induce a strong local electric field. The results show that incorporating nanoparticles in the ICL improves the prospects for achieving highly efficient polymer-based solar cells.



Silver Trimolybdate Wires Could Be Golden for Numerous Applications

Metal molybdates have interesting properties that are being explored for a variety of applications in fields such as photoluminescence, optical fibers, and catalysts. Silver molybdates, in particular, have attracted attention for their potential applications in conducting glass and ammonia sensing. Although most synthesis methods for silver molybdates rely on a straight and harsh reaction in a molybdenum trioxide/silver oxide system, researchers are increasingly exploring solution-based synthesis and the applications of these resulting materials. However, little is known about some pivotal properties of silver trimolybdates resulting from solution synthesis, including phase transformation, thermal stability, and photocatalytic and optical characteristics.

To explore these properties, Feng *et al.* (DOI: 10.1021/nn202296h) embarked on a systematic study using silver trimolybdate nanowires they synthesized using a simple hydrothermal process. Scanning electron microscopy and high-resolution transmission electron microscopy showed high-quality nanowires that were several hundred micrometers long. Using various tools to investigate phase transformation at a range of temperatures revealed strong thermal stability. Similarly, photoirradiation revealed strong light stability, while also providing evidence of aggregating isolated silver ions into silver clusters that showed up in microscopy as beads on the wires. Using the degradation of RhB as a model reaction, the researchers show that the as-grown nanowires show clear photocatalytic activity, which increases after the nanowires are photoirradiated. These nanowires also showed potential for surface-enhanced Raman spectroscopy, using rhodamine 6G as a model molecule, as well as good electrical conductivity. This exploration suggests that silver trimolybdate nanowires could have numerous practical applications in photocatalysis, microelectrodes, or sensors.



A New Slant on ZnO Nanogenerators

As a proliferation of useful nanoscale devices come closer to fruition, researchers are becoming increasingly interested in finding power sources to drive these devices without adding volume. Consequently, piezoelectric nanogenerators that can harness the mechanical energy of body movements, heartbeats, or acoustic waves, for example, are attracting increasing attention. ZnO's biocompatible, degradable, and nontoxic nature, as well as its simple synthesis and low cost, make it one of the most promising materials for constructing nanogenerators. However, most studies have focused on understanding vertically oriented ZnO nanowires arrays, with little focus on the effects of other orientations.

To understand this material and bring ZnO-based nanogenerators closer to realization, Chen *et al.* (DOI: 10.1021/nn202251m) studied ZnO nanowires synthesized using oblique-angle deposition and hydrothermal growth, resulting in arrays tilted 20° relative to the substrate normal. The researchers then examined the piezoelectric response of these arrays using an atomic force microscope in contact mode, scanning the arrays and bending the nanowires in four different directions. To increase the measured voltage signal in these tilted arrays, the researchers used a highly conductive Al-doped ZnO layer as the bottom electric contact. While the average piezoelectric voltages were nearly identical in sweeps performed in both directions perpendicular to the azimuthal tilt direction, the researchers found that along or opposite to the tilt direction, outputs were significantly lower and differed by up to 20 mV depending on direction. The findings suggest that piezoelectric output from ZnO nanowires arrays can depend significantly on orientation, providing a foundation for improving the performance of nanogenerators.