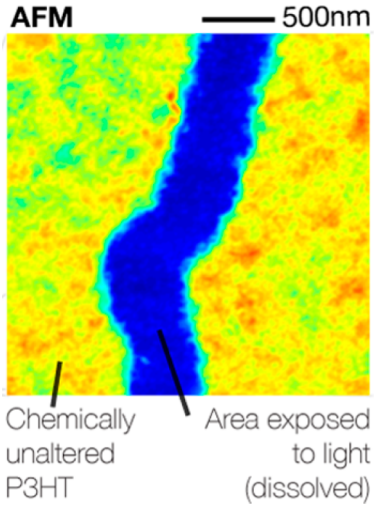
The Straight Dope on Synthesizing Organic Electronics

Interest in organic electronics has grown in recent years due to the potential to tune material properties chemically and to manufacture large-area devices inexpensively through solution processing. While products taking advantage of chemical tunability have already hit the marketplace, those produced by solution processing have lagged. Because most conjugated organic materials are miscible, nearly all commercial organic electronics are currently manufactured by comparatively costly vacuum deposition techniques, limiting material choices to small molecules or oligomers.

In a step toward solution processing, Jacobs *et al.* (DOI: 10.1021/nn506820d) developed a way to change the solubility of polymers reversibly, making them candidates for use in organic electronics. The researchers did this by doping semiconducting polymers with high electron affinity molecules, a technique they dubbed dopant-induced solubility control

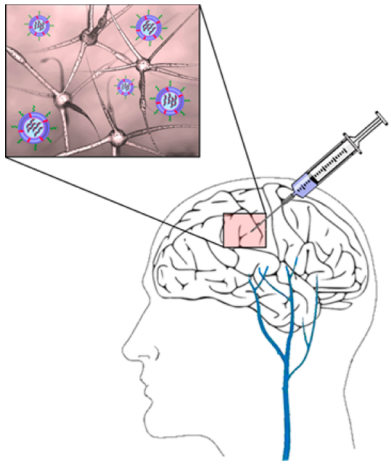


(DISC). They demonstrated the feasibility of this technique using the semiconducting polymer poly(3-hexylthiophene) (P3HT). When mixed with a molecular dopant, P3HT becomes insoluble in a wide range of solvents, allowing it to be successfully layered on another semiconducting polymer. The researchers demonstrated that the dopant could be removed with light or immersion in a dedoping solution, allowing complex patterning by either adding dopants and dissolving away undoped areas or starting with a universally doped polymer film and using light to write patterns. Tests showed that after forming these structures, removing the dopant did not affect the optical characteristics, charge carrier mobilities, or nuclear magnetic resonance spectra. The authors suggest that DISC might be expanded to other classes of materials, making other conjugated organic materials candidates for organic electronics.

Getting siRNA into Glioblastoma

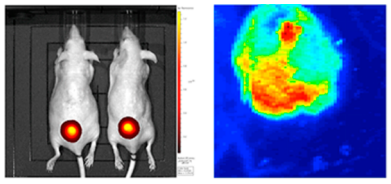
Glioblasoma multiforme (GBM) is one of the most devastating human cancers, with median survival under current standards of care of just over a year from diagnosis. Although chemotherapy and radiation can extend life by weeks to months, GBM's severely aggressive and infiltrating nature has thus far thwarted attempts at inducing long-term remission. Despite these disappointments, recent studies have showcased the potential of nanoparticles carrying various drugs or metabolites to change the course of GBM.

Following this trend, Cohen *et al.* (DOI: 10.1021/nn506248s) developed a way to deliver siRNA targeting GBM tumors using nanoparticles. To get this agent into cells effectively, the researchers coated lipid-based nanoparticles with hyaluronic acid (HA), a naturally occurring glycosaminoglycan that serves as the major ligand of the CD44 receptor, which tends to be overexpressed or constitutively expressed on many types of cancer cells. Using siRNA against PLK1, a gene thought to play an important role in GBM and other cancers, the researchers loaded these nanoparticles and tested their activity against GBM both *in vitro* and *in vivo*. Results showed that the HA-coated nanoparticles bound to glioma cells and effectively delivered their payload, inducing cell death. In a mouse xenograft model, the treatment nearly tripled the length of survival in 60% of the animals compared to those who received a different siRNA, the longest ever reported survival of mice in this orthotopic GBM model. The authors suggest that this modality might offer an effective new treatment against GBM.



Watching Lithium in Real Time

Medical imaging is one of the key pillars of personalized medicine. However, conventional optical imaging techniques suffer from several drawbacks, including limited penetration depth of light and loss of spatial resolution in deep tissues from scattering. Although photoacoustic imaging can mitigate these problems, achieving imaging depths of several centimeters and better spatial resolution, most developed techniques have focused on imaging endogenous molecules or exogenous contrast agents. Few photoacoustic approaches have used this tool to monitor changes in analyte concentrations deep within intact tissues.



In a new study, Cash *et al.* (DOI: 10.1021/nn5064858) illustrate a new system to monitor lithium photoacoustically and fluorescently simultaneously, offering a way to compare these measurements. Because lithium, a common treatment for bipolar disorder, has both a narrow therapeutic window and a low toxic dose, it offers a valuable model system for testing photoacoustics to monitor analyte concentrations. To synthesize their nanosensors, the researchers placed a lithium-selective crown ether ionophore into the core of polymeric nanoparticles, causing both the absorption spectrum and fluorescence intensity of the nanoparticles to change with lithium concentration. *In vivo* tests in a mouse model showed that photoacoustic imaging was significantly more sensitive than fluorescent imaging after lithium was administered to the animals through intraperitoneal injection. The authors note that this technique offers the first real-time tracking of lithium concentrations without blood sampling and provides measurements deep within capillary beds that have been previously unattainable, characteristics that could have a profound effect on chronic disease management.

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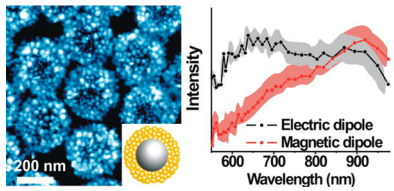
Giving Metamolecules the Raspberry

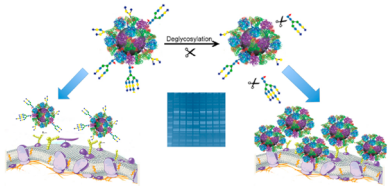
Theoretical studies have suggested that subwavelength metal nanoparticles arranged in three-dimensional clusters can support magnetic resonances at optical frequencies. Deemed "metamolecules," these clusters have a bevy of exciting potential applications including plasmonic cloaking, superlenses, and enhanced nonlinear optical properties. Recently, several groups have developed approaches for creating metamolecules with magnetic resonances. However, to create even stronger magnetic resonances, researchers must develop a method that reduces the interparticle distance but also prevents the individual particles composing these structures from touching each other, a feat difficult to achieve with most self-assembly techniques.

Qian *et al.* (DOI: 10.1021/nn5050678) report a new synthetic approach that accomplishes this goal. Using a seed-growth method that starts with polystyrene cores decorated with silver seeds, the researchers grew gold nanobeads. An aromatic surfactant in the growth solution prevented these nanobeads from fusing together, causing the resulting structures to resemble raspberries. Various analyses, including finite difference time domain simulations and experimental studies, showed that the particles exhibited unprecedentedly strong magnetic dipole scattering as a result of this structure. Additionally, the optical properties of these raspberry-like metamolecules could be tuned both by varying the size of the core, which affects the number of nanobeads per cluster, and the size of the individual nanobeads. The authors suggest that the facile fabrication, tunability, and strong magnetic properties of these particles could make magnetic metamaterials more accessible for promising future applications.



Sugar-Free Protein Coronas Show Importance of Glycosylation

Nanoparticles have earned a prominent role in a broad range of biomedical applications, including imaging, research, and therapeutics. For the continued development of this field, researchers must gain a better understanding of the complex interactions between nanoparticles and biological systems. One important aspect of these interactions is the adsorption of biomolecules onto the surfaces of nanoparticles, forming an interface known as the protein corona. Numerous studies have shown that this coating modulates many facets of nanoparticle–cell interactions, including mobility and toxicity. Although the molecular composition, structure, conformation, and organization of proteins in this corona is critical for determining exactly how nanoparticles interact with cells, researchers still know little about the role of glycosylation, the post-translational addition of various sugars.

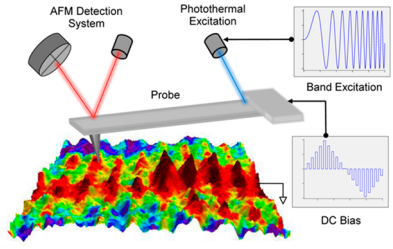


To investigate, Wan *et al.* (DOI: 10.1021/nn506060q) probed how glycosylation affects nanoparticle–cell interactions by comparing nanoparticles with typically glycosylated protein coronas with those that had been deglycosylated. Using protein coronas derived from human plasma, a rich source of heavily glycosylated proteins, the researchers showed with sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) that deglycosylation using a glycosidase mixture caused an increase in the corona proteins' electrophoretic mobility. Further studies showed that the glycosidase mixture removed some glycan groups on the surface, exposing internal ones. These internal glycans increased nanoparticle adhesion and uptake in two different types of macrophages, leading to the production of pro-inflammatory cytokines. The authors suggest that these results illustrate the importance of glycosylation for nanoparticle–cell interactions.

Picking Up Good Vibrations

Contact resonance atomic force microscopy (CR-AFM) is often used to measure a material's mechanical properties. In this method, the cantilever tip is usually excited with a piezoelectric transducer, which allows the local elastic properties of samples to be measured down to the nanoscale. Although CR-AFM has been widely applied in diverse materials including polymers, minerals, and biological samples, it has significant shortcomings, including finding a clean, broadband, and versatile excitation manner. Piezoelectric excitation can produce noise and spurious coupling effects, particularly in a liquid environment. Additionally, spectroscopic modes for CR-AFM have not been significantly explored, limiting this modality to static imaging measurements.

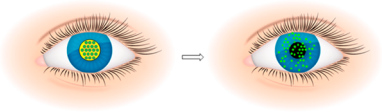
In a new study, Li *et al.* (DOI: 10.1021/nn506753u) develop a methodology to address these shortcomings by not only introducing photothermal excitation to CR-AFM, but combining it with contact resonance voltage spectroscopy based on an existing set of band excitation spectroscopies. Using this novel modality, the researchers explored local bias-induced phenomena in a variety of materials. In a sputtered lead zirconate titanate (PZT) thin film across the PZT/SiO_2 boundary, they showed a clear material contrast between the two materials. On an epitaxial PZT film, there were small but detectable stiffness changes during local polarization switching processes. Using this method to probe the Si nano-oxidation process, the researchers found remarkably high contact resonance frequency shifts during an early stage of the reaction when SiO_2 was not fully formed, suggesting the high sensitivity of this method to detect local, irreversible electrochemical processes. Eventually, the authors suggest, CR-AFM could be further extrapolated to probe the nanomechanical behavior of materials under other types of applied stimuli.



Drug-Delivering Nanowafers: More than Meets the Eye

About 2.5 million eye injuries occur each year in the United States alone. Because injuries to the ocular surface can trigger corneal neovascularization (CNV), causing blood vessel growth into this normally avascular structure, these injuries constitute a major cause of blindness. Various drugs can be delivered to the ocular surface to thwart this process. However, ocular drug delivery's potential is hampered by the eyes' unique barriers, including reflex tearing, constant blinking, tight epithelial junctions at the ocular surface, and nasolacrimal drainage that rapidly clears eye drops. Thus, topical eye drops need to be applied several times a day, which increases the risk for toxic side effects including cellular damage, inflammation, and blurred vision, all of which can decrease patient compliance.

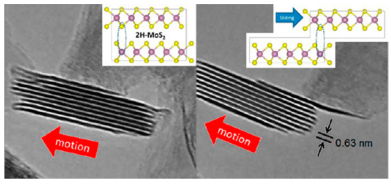
Seeking a better way to deliver drugs to the ocular surface, Yuan *et al.* (DOI: 10.1021/nn506599f) developed a nanowafer that sits on the surface of the eye to deliver drugs slowly from nanoreservoirs, increasing the residence time of therapeutics on the ocular surface. After testing various polymers, the researchers settled on poly(vinyl alcohol) (PVA) as the main component of the nanowafers because it did not stimulate the expression of proinflammatory and proangiogenic factors. After loading nanoreservoirs in disc-shaped PVA nanowafers with axitinib, a tyrosine kinase inhibitor already shown to slow or to reverse CNV, the researchers show in an ocular burn model that axitinib significantly inhibited CNV and improves corneal wound healing. The authors suggest that this simple and effective system could constitute a new and better way to deliver drugs to the ocular surface.



Molybdenum Sulfide Does the Electric Slide

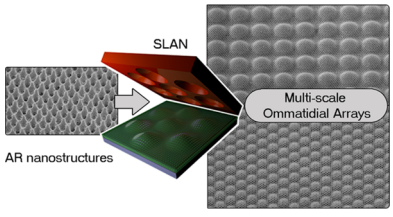
Researchers have long studied the tribology of MoS_2, a common layered compound often used as a dry lubricant. The lubricating properties of MoS_2 derive from the low strength of its interplanar van der Waals bonds compared to the basal plane covalent bonds, which allows its planar layers to slide easily under shear stress. Although that much is known, gaining a better understanding of this process at the nanoscale has been hampered by difficulties in applying proper shear stress to the interlayer interface of a single microscopic flake of this layered material and technical problems with observing the interlayer sliding process in a cross-sectional view.

In a new study, Oviedo *et al.* (DOI: 10.1021/nn506052d) developed methods to achieve interlayer sliding in MoS_2 while observing these motions with a transmission electron microscope (TEM). Starting with bulk MoS_2 flakes, the researchers electrostatically coupled these materials to a tungsten probe with a thick native oxide layer attached to a micromanipulator under a high dc electrostatic bias. This method allowed them to tear small nanoflake pieces and to observe interlayer sliding in cross section. These experiments showed the appearance of a periodic negative sliding potential energy barrier when the layers slide into the out-of-registry stacking configuration, suggesting that electrostatic gating can modify the interlayer tribology of this material. The researchers also demonstrated that MoS_2 could be sheared with a nanoindenter force sensor, using this method to measure the zero normal load shear strength. The authors suggest that these experiments can shed light on the atomic mechanisms from which the interlayer sliding of MoS_2 originates.



A New Way To Mimic Moth Eyes

The unique structures of the eyes of various organisms have provided much inspiration for design aspirations. Of particular interest are the eyes of moths, which constitute a curvilinear design of hexagonally packed microlenses called ommatidia. The ommatidia themselves are textured into patterns of hexagonally packed structures that confer antireflective abilities, enabling these nocturnal creatures to have superior night vision capabilities even in the dimmest starlight. Moreover, these patterns also provide an antifogging capacity that further helps focus light. Although researchers have sought to replicate these abilities by copying the ommatidial design of moth eyes, they have thus far been unsuccessful in developing a method for fabricating these arrays on large-area substrates using a simple and scalable technique, which would be necessary for the large-scale manufacturing required for commercial applications.



In a new study, Raut *et al.* (DOI: 10.1021/nn5051272) introduce a method called sacrificial layer mediated nanoprinting (SLAN) that accomplishes these goals. Based on nanoimprint lithography (NIL), this method first fabricates the ommatidial nanostructure patterns on a polycarbonate film, followed by imprinting the microlens arrays. However, differing from NIL, SLAN uses a sacrificial layer of poly(sodium 4-styrenesulfonate) (PSS) during this imprinting to encapsulate the nanostructure patterns and to prevent deformation of the nanostructures. The PSS could then be rinsed off in water after the mold release. Analysis showed that patterns were transferred with high fidelity over large surfaces, demonstrating low reflectance, superhydrophobicity, and antifogging capabilities. The authors suggest that these arrays could find application in image sensors, solar cells, LEDs, and numerous other micro-optic components.