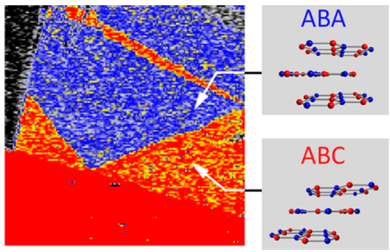
How Graphene Stacks Up

Different stacking configurations in few-layer graphene (FLG) can dramatically vary the properties of this material, particularly, in trilayer graphene. Depending on the configuration of its three layers, this material can assume a Bernal structure with an "ABA" pattern, which is semimetallic, or a rhombohedral structure with an "ABC" pattern, which is semiconducting. Better understanding of these stacking-specific properties in FLG could benefit both basic science as well as the development of new electronic and optoelectronic devices with adjustable band gaps. Because FLG samples are usually composed of domains with different stacking orders, researchers must employ powerful microscopy or spectroscopy techniques to investigate the formation and interconversion of stacking orders, the structures of stacking domain boundaries, and their influence on transport properties. Although high-resolution microscopy, scanning tunneling microscopy, and far-field infrared spectroscopy have all been used to explore these questions, each technique has drawbacks that limit its usefulness.

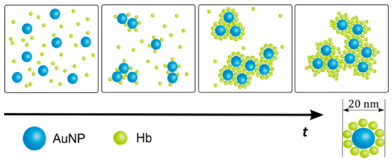
In a new study, Kim *et al.* (DOI: 10.1021/acsnano.5b02813) investigated the use of infrared scattering scanning near-field optical microscopy (sSNOM) to visualize and to characterize the stacking domains in FLG at the nanometer scale. Measuring the scattering from a laser-illuminated junction between the metallic tip of an atomic force microscopy probe and the sample surface, the researchers found stacking-specific sSNOM contrast in mechanically exfoliated FLG on a SiO_2/Si substrate. Combined with modeling, the researchers were able to assign domains as Bernal, rhombohedral, or intermediate stacks for TLG and stacks with up to five layers clearly. The authors note that this promising technique allows greater experimental flexibility than techniques previously used to investigate FLG.



Gold Nanoparticles and Proteins Gain Their Cluster

As the use of nanoparticles in medicine gained momentum, researchers learned that proteins can interact with dispersed, charged nanoparticles, acting as complex surfactants. Protein adsorption onto the nanoparticle surface can decrease or increase the nanoparticles' colloidal stability, leading to agglomeration or stable dispersion under various circumstances. One example of this phenomenon is citrate-stabilized Au nanoparticles (AuNPs), which agglomerate in the presence of hemoglobin (Hb) at acidic pH. These mixtures tend to remain stably dispersed at very low and very high ratios of Hb to AuNPs, with full agglomeration and precipitation occurring at a ratio that corresponds to a Hb monolayer on the AuNP. However, at just above and just below this value, stable, microscopic AuNP–Hb clusters form, a phenomenon that is not well understood.

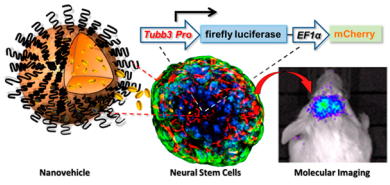
To investigate, Moerz *et al.* (DOI: 10.1021/acsnano.5b01043) used dynamic light scattering and surface acoustic wave phase measurements to probe agglomerate growth kinetics and stability and to analyze Hb adsorption kinetics on Au surfaces. Combining these data with a modified Smulochowski agglomeration model, the researchers developed an explanation for this complex behavior. Their results suggest that clusters form at slightly higher than monolayer [Hb]/[AuNP] ratios when partial multilayers form and act as spacers between the Au cores and decrease van der Waals attraction. At slightly lower ratios, small protein patches, potentially single proteins, bridge individual AuNPs, allowing them to form clusters. The authors suggest that this model could apply to other particle–protein combinations and could be applicable to estimating the effects of nanoparticle release in aquatic environments or the dispersion of nanoparticles in the human body.



Nanovehicles Help—and Watch—the Central Nervous System Heal

Stem cells continue to attract attention for their therapeutic potential, particularly, in regenerative medicine as replacements for damaged or dysfunctional tissues and organs. Recently, this promise has extended to neural stem cell (NSC) transplantation, which has shown enormous promise in alleviating central nervous system damage, including restoring brain function after diseases or injuries. Although the ultimate fate of NSCs used to treat some neural disorders has been investigated, how these cells differentiate spatially and temporally and how they interact with the stem cell niche in the adult brain remains virtually unexplored. Researchers also lack a reliable way to control the differentiation of transplanted NSCs into specific neural subtypes.

Seeking a solution to both problems, Wang *et al.* (DOI: 10.1021/acsnano.5b00690) developed a polymeric nanovehicle for sustained release of a morphogen that promotes neuron development, and they constructed a bicistronic vector with a unique neuron-specific gene promoter that drives reporter gene expression to image NSC differentiation and migration in real time. Tests showed that the nanovehicle, made of biodegradable polyesters, enabled efficient NSC uptake and sustained release of retinoic acid directly into the cytosol to drive differentiation into neurons. Combining their efforts with the promoter, the researchers witnessed migration, proliferation, differentiation, and apoptosis regulated by nanovehicles in a mouse model of traumatic brain injury. Although only a few NSCs migrated to the lesion and differentiated into neurons, these functionally ameliorated the impact of the injury. The authors suggest that both advances could eventually benefit neuronal regenerative medicine.



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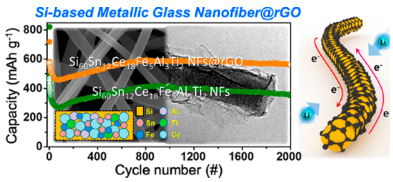
Anodes for Li-Ion Batteries: All Wrapped Up

Si has been extensively explored as an anode for Li-ion batteries due to its high theoretical capacity, which is about 11 times higher than commercial graphite anodes. However, the extreme volume changes that crystalline Si undergoes during cycling cause it to fracture and ultimately pulverize. These severe expansions and contractions also rupture the solid-electrolyte interphase (SEI) layer that forms on the Si electrode surface during cycling. These two circumstances lead to the formation of an irregular SEI layer, which leads to a significant increase in the cell resistance and, eventually, deterioration of the cell capacity and degradation of the cycle performance. To ameliorate these deficits, amorphous silicon (a-Si)



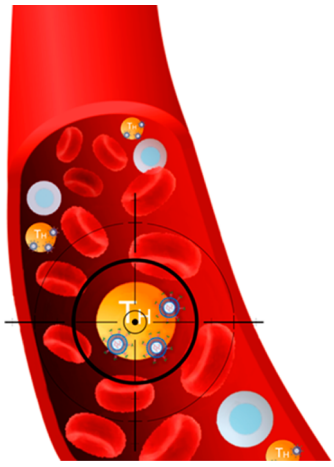
has been explored as an alternative anode material due to its less severe volume changes after full Li^+ insertion.

In a new study, Jung *et al.* (DOI: 10.1021/acsnano.5b01402) test the feasibility of this approach to create Li-ion battery anodes with the potential for ultralong cycle life. The researchers used electrospinning to create a-Si-based metallic glass alloy with the formula $Si_{60}Sn_{12}Ce_{18}Fe_5Al_3Ti_2$. To test its performance as an anode, the investigators incorporated this material in coin-type half-cells with Li counter electrodes. Tests showed reversible capacity retention nearly 2.7 times higher than that of conventional graphite anodes and excellent cycling capabilities for nearly a year and hundreds of cycles. They then wrapped these nanofibers with graphene to stabilize the electrochemical interface further, thereby improving the Coulombic efficiencies and cycle life. The authors suggest that this novel material could significantly improve the performance of Li-ion batteries.

Shushing Genes with Lipid Nanoparticles

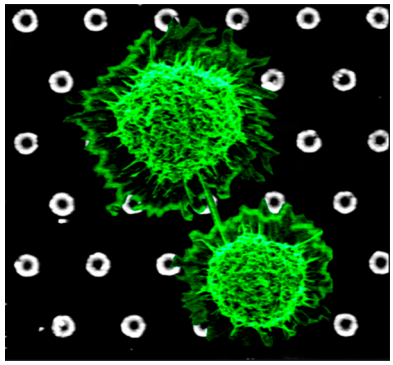
$CD4^+$ T lymphocytes interact with antigen-presenting cells and secrete cytokines to regulate and to balance the inflammatory response. When this functionality goes awry, it can contribute to a variety of immunological disorders, including excessive inflammation, cancer, autoimmunity, and viral infections. Consequently, these cells have become an attractive target for a variety of therapeutic interventions. Although RNA interference (RNAi) technology has proven useful for silencing genes in many different cell types for research and therapeutic applications, immune cells are notoriously difficult to transfect. Finding a way to deliver the small interfering RNAs (siRNAs) that silence genes in RNAi has thus far proven to be a major hurdle toward adopting this technology for $CD4^+$ T lymphocytes.

In a new study, Ramishetti *et al.* (DOI: 10.1021/acsnano.5b02796) demonstrate a way to transfect this cell population with siRNA using targeted lipid nanoparticles (LNPs). The researchers created these LNPs using the NanoAssemblr microfluidic mixing device by mixing acidified siRNAs against the cell surface tyrosine phosphatase CD45, a pan leukocyte marker, with a variety of lipids, producing LNPs that encapsulated the siRNA at a nearly 100% efficiency. They then conjugated monoclonal antibodies against CD4 to a functional group on the LNP surface. Tests show that these targeted LNPs successfully delivered siRNAs into $CD4^+$ cells and silenced CD45 in blood circulating $CD4^+$ T cells and a variety of other hematopoietic organs, including spleen and blood marrow. Subsequent tests showed that only a subset of $CD4^+$ cells internalized the LNPs and became functionally silenced. The authors suggest that gaining a better understanding of this limitation could lead to maximal silencing in T lymphocytes.



Helping Cells Connect with Haptens

Many cell types, including a variety of neuronal and immune cells, produce membrane nanotubes. These structures connect two or more cells, providing membrane continuity and enabling intercellular exchange of membrane-carrying molecules and cytoplasmic content. Membrane nanotubes play an important role in a variety of physiological processes including immune defense, tumorigenesis, transmission of pathogens, and cell differentiation. Recently, researchers showed that it was possible to prompt bone-marrow-derived mast cells to produce membrane nanotubes by using an antigen and a ligand to costimulate two receptors: the FcεRI receptor and the chemokine receptor (CCR1). Although rat basophilic leukemia (RBL) cells are often used as models for mast cells, this co-stimulatory approach did not prompt them to



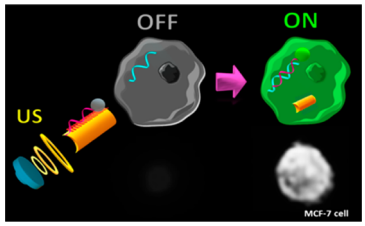
produce membrane nanotubes as they lack the CCR1 receptor.

Seeking a new method for membrane nanotube production in this cell type, Li *et al.* (DOI: 10.1021/acsnano.5b02270) used haptens of 2,4-dinitrophenyl (DNP) molecules. These molecules were presented as uniform arrays of nanorings on silicon substrates, with nanorings differing in diameter and spatial arrangement between arrays. After exposing RBL cells to these haptens, microscopy images showed various assemblies of membrane nanotubes connecting cells, including single bridges between individual cells, multiple bridges between individual cells, and bridges connecting single cells to several others. Comparing the hapten arrays to self-assembled monolayers of DNP, the researchers showed that the local presentation of DNP appeared to be responsible for membrane nanotube formation. The authors suggest that nanotechnology such as this can offer a new platform to activate desired cellular signaling cascades selectively despite failures of current technologies.

Taking microRNA Sensing for a Test Drive

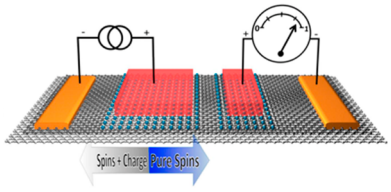
Non-protein-coding RNA known as microRNA (miRNA) has long offered a useful way to modify gene expression to study early development, cell differentiation, hematopoiesis, and proliferation. Additionally, because their abnormal expression has been associated with a variety of conditions ranging from cancer to diabetes, miRNAs can be useful biomarkers for disease diagnosis and therapy. Consequently, finding ways to detect the presence and abundance of specific miRNAs could be of considerable clinical importance. Several different methods have been used for this purpose, including Northern blotting; real-time quantitative PCR; microarrays; and electrochemical, fluorescence, or electrochemiluminescence sensors. However, these have significant drawbacks, such as requiring long incubation times and high cell densities.

In a new study, Esteban-Fernández de Ávila *et al.* (DOI: 10.1021/acsnano.5b02807) report a new miRNA sensing approach that utilizes ultrasound-guided nanomotors. To craft these nanomotors, the researchers coated cysteamine-modified gold nanowires with graphene oxide. To this assembly, they adsorbed a fluorescent dye-labeled single-stranded DNA probe with preferential binding for miRNA-21, an miRNA that is found to be overexpressed in 80% of tumor samples. Interaction with the graphene oxide quenched the fluorophore. However, when the probe bound with its miRNA-21 target, it rapidly recovered its fluorescence. Tests in a breast cancer cell line with abundant miRNA-21 and HeLa cells with low miRNA-21 showed the feasibility of this approach for detecting and quantifying miRNA down to the single cell level. The researchers suggest that this approach could eventually be expanded to clinical use for a variety of other endogenous biomarkers, including siRNAs, piRNAs, or proteins.



Taking Hydrogenated Graphene for a Spin

Theoretical values for graphene's spin lifetime and spin diffusion length based on its low atomic number and spin−orbit coupling make this material a natural choice for the next generation of low-power, high-performance spintronic devices. However, reported values still remain far from graphene's theoretical limits. Research suggests that several sources of scattering could be responsible for the experimentally observed lower spin lifetimes, including scattering caused by charges in the substrate, grain boundaries, defects and impurities in the graphene or at contacts, and scattering introduced by the tunnel barrier, a topic just attracting attention. Although investigators recently reported that a fluorinated graphene tunnel barrier structure



produced the highest spin polarization ever achieved in graphene, this operation was not achieved at room temperature, and this material has reduced stability compared to conventional dielectric materials.

Seeking to overcome these issues, Friedman *et al.* (DOI: 10.1021/acsnano.5b02795) tested hydrogenated graphene as a homoepitaxial spin tunnel barrier. Using graphene grown by chemical vapor deposition, the researchers created four-layer stacks on SiO_2/Si substrates and then hydrogenated the top layers to create a tunnel barrier. After four-terminal nonlocal spin valve structures were fabricated, measurements on this device showed electrical spin injection, transport, precessional dephasing, and detection in the lower graphene channel layers. Although spin lifetimes were stable regardless of temperature, spin polarization efficiencies were significantly lower than those measured in fluorographene tunnel barriers, a factor the authors say could stem from the presence of magnetic moments in the hydrogenated graphene that act as spin scatterers. Regardless, they suggest that these results show hydrogenated graphene as a reasonable candidate for future spintronic devices.

Limits of Storage, From Crystalline to Amorphous

Phase-change materials' (PCMs) nonvolatility, high operating speed, scalability, and cyclability have positioned them as promising candidates for use as active media in universal data storage devices. Rather than relying on electrical charges for encoding information, as current commercial devices do, PCMs instead exploit the large differences in physical properties between their multiple structural phases. This crucial difference makes data leakage negligible for PCMs, substantially increasing storage density. Gaining a better knowledge of PCMs could help researchers improve the performance of these materials, which is ultimately governed by the speed limit of transformation among their different phase structures.

In a new study, Hu *et al.* (DOI: 10.1021/acsnano.5b01965) use ultrafast electron crystallography to evaluate the lattice evolution of crystalline GeTe nanofilms, a prototypical PCM whose structure has been well-defined and characterized. After delivering a 120 fs laser pulse, the researchers monitored the temporal behavior of the measured positions and intensities of Bragg reflections. Their findings show that within 12 ps, this material transitions from an initial rhombohedral phase to an intermediate cubic, or rocksalt-type structure. Further investigations suggest that this phase transition is mediated by both electronic and structural instabilities. On a much longer time scale of hundreds of picoseconds, depending on film thickness, this material reaches the thermal equilibrium that drives this system toward its final amorphous state. The authors suggest that studies such as this one could help researchers determine the limits of performance of various PCMs, a key to developing these materials for high-speed recording applications.