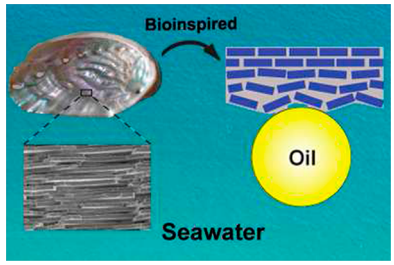
Mother of Pearl-Inspired Material Gives Oil Wide Berth

With the frequent occurrence of accidental oil spills in marine environments, superoleophobic coatings that prevent oil fouling under seawater are becoming an increasingly popular research focus. However, traditional fluorinated superoleophobic coatings lose their oil repellency in water, making them unsuitable for this application. The recent discovery of oil-repellant properties in fish scales and clamshells suggest a new way to solve this problem with high-surface-energy materials, such as polymer hydrogel or copper oxide coatings. However, these coatings suffer from mechanical problems that limit their use; for example, hydrogels are subject to collapse and deformation, and these and other underwater superoleophobic films are easily damaged by fluid flush in seawater and scraping or rubbing from sand. One material with excellent mechanical properties that researchers might mimic for creating a resilient coating is mother of pearl, or nacre, the lustrous inner shell layer of some mollusks.

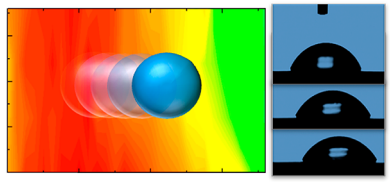
In a new study, Xu *et al.* (DOI: 10.1021/nn400650f) report the synthesis of a nacre-like coating that is extremely durable and superoleophobic under water. The researchers created this coating with layer-by-layer assembly, using chitosan-montmorillonite clay as "bricks" and the polyelectrolites poly(4-styrenesulfonic acid) and poly(diallyldimethylammonium chloride) as "mortar," mimicking the bricks-and-mortar design of nacre. Tests show that this material readily repels droplets of a variety of different oils. Nanoindentation and sand abrasion did not affect the superoleophobic quality of this resilient material. The authors suggest that this new coating could be used for marine antifouling or microfluidic applications.



Pushing and Pulling Droplets with Functionalized Graphene

Pristine graphene's unusual electrical, optical, thermal, and mechanical properties have inspired a vast amount of research. However, scientists are increasingly studying how this material can be modified to enhance its capabilities. Previous research has shown that various tweaks to this material's surface chemistry can significantly change its native properties, including graphene's wettability, a property critical for a variety of other applications. When applied in a gradient, functional groups that affect wettability can direct the flow of liquid droplets. However, precisely applying functional groups in both the *x* and *y* axes so that adsorbates will move in the desired direction without being pinned has proven to be a delicate task.

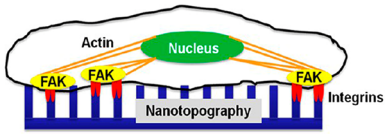
In a new study, Hernandez *et al.* (DOI: 10.1021/nn304267b) use plasma to apply a high-quality gradient of oxygen- or fluorine-rich functional groups on graphene that either pull or push droplets of water in a directed fashion. To achieve these gradients, the researchers used a canopy-shaped mask, which allowed a gradual decrease in plasma concentration farther underneath the canopy. Adjusting the canopy's height, length, and thickness tailored the density of the applied functional groups. Raman, micro-Raman, and X-ray photoelectron spectroscopy verified the existence of functional group gradients on graphene. Tests showed that these functional groups successfully changed the surface's interaction with liquids, causing droplets of water or dimethyl-methylphosphonate to roll in the direction of increasing oxygen content or roll away from increasing fluorine content. The authors suggest that such tunable surface chemistry could be used in applications such as microfluidics or chemical sensing.



Why Nanotopography Directs Stem Cell Differentiation

Researchers have long known that multipotent stem cells rely on a bevy of cues from the extracellular matrix, including topographical and biochemical signals, to guide tissue development. Both micro- and nanoscale topographical structures have been shown to influence proliferation, migration, endocytosis, and differentiation. Although the effects of these physical cues have received significant attention, the mechanism behind these effects has been unclear.

Providing some new insight, Teo *et al.* (DOI: 10.1021/nn304966z) show in a variety of experiments that nanotopography-induced differentiation of human mesenchymal stem cells (hMSCs) is controlled at least in part by the integrin-activated focal adhesion kinase (FAK). The researchers



plated hMSCs on polydimethylsiloxane substrates patterned with nanogratings with 250 nm line widths. Within a week of plating, these cells developed aligned stress fibers and showed markers of neurogenic and myogenic differentiation. Their focal adhesions were significantly smaller and more elongated than cells plated on unpatterned substrates or even those with microgratings. By inhibiting or enhancing actomyosin contractility, the researchers show that regulation of differentiation is directly force dependent. Further investigation showed that FAK phosphorylation is necessary for this topographically influenced hMSC differentiation and that overexpressing FAK overruled topographical cues in guiding cell lineage. The authors note that these findings demonstrate the importance of FAK in topography-induced differentiation. However, they add that further research will be necessary to understand the roles of other cellular components in guiding stem cell fate.

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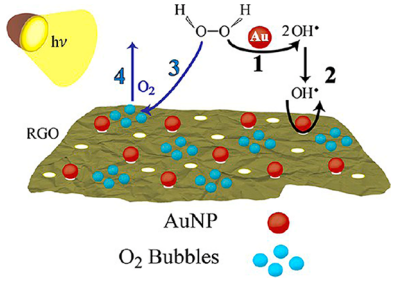
The "Holey Grail" for Reduced Graphene Oxide

Graphene oxide (GO) lends itself more easily than graphene to functional composites because single sheets of this material are more readily dispersed in water and other solvents. Graphene oxide is inherent electrically insulating, but can be modified to restore conductivity partially through reduction. Thus, use of reduced graphene oxide (RGO) has been explored in a variety of applications where this property is particularly valuable, such as energy conversion or storage systems. The built-in wrinkles in RGO aid diffusion of ions through natural tunnels, edges, and macropores, facilitating three-dimensional electrode designs. By creating intentional pores, this material's surface area can be increased even further, improving the diffusion of electroactive species.

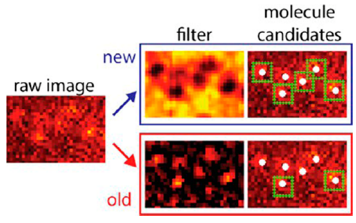
Radich and Kamat accomplish this goal in a new study (DOI: 10.1021/nn401794k) by creating nanopores in RGO through the generation of hydroxyl radicals catalyzed by gold nanoparticles (AuNP). The researchers placed RGO in suspensions containing H_2O_2 or AuNPs alone or together, then exposed the solutions to UV light, which caused the generation of highly reactive $OH^{\bullet}$ radicals in solutions containing H_2O_2. Several different characterization methods showed that solutions containing both H_2O_2 and the catalyzing AuNPs produced the most significant changes in RGO, leading to a new material that the authors dubbed oxidized RGO (ORGO) with a heavily wrinkled and pored morphology. With longer irradiation times, the researchers propose that AuNPs may continue to migrate, helping to form increasing numbers of holes in ORGO. They suggest that this method could produce a material with tunable properties while also enabling understanding of RGO oxidation in applications where free radicals are expected to form.



Shining a New Light on Super-Resolution Fluorescence Microscopy

Thanks to recent advances, the spatial resolution limit of super-resolution fluorescence microscopy is now down to tens of nanometers, providing an unprecedented view of structural detail in biological systems. One widely used approach is the stochastic switching method, which includes the techniques known as (fluorescence) photoactivation localization microscopy ((F)PALM) and stochastic optical reconstruction microscopy (STORM). This method excites just a few, sparsely distributed fluorophores in a field of view. By acquiring thousands of repeated images and analyzing them with specialized software to localize the activated molecules, researchers can produce a final image with a resolution far below the diffraction limit. Although researchers have devoted significant attention to improving molecular localization, far less attention has been paid to improving initial molecular detection.

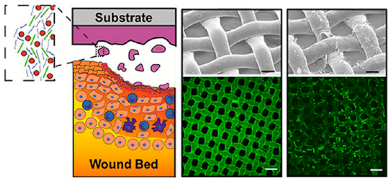
Focusing on this neglected first step, Li *et al.* (DOI: 10.1021/nn4009388) developed a new molecular detection algorithm that greatly improves molecule detection efficiency while minimizing false detection that causes image artifacts. Their novel algorithm—which they named accurate live-PALM (a-livePALM)—and the leading conventional method both first convolute raw images with a Gaussian kernel to enhance signal while reducing noise. Whereas the conventional method sets a threshold based on the signal-to-noise ratio, a-livePALM performs additional local contrast enhancements using an adaptive histogram equalization technique. Simulations and tests with real images suggest that this new algorithm identifies molecules more efficiently and reliably than several other publicly available programs. The authors suggest that this new detection method could be useful for a variety of scenarios for super-resolution microscopy.



Dressing siRNA for Success

The technology known as small interfering RNA (siRNA), which knocks down gene function using short snippets of double-stranded RNA molecules, has proven enormously useful in basic molecular biology. Researchers have studied its utility in medicine as well; however, siRNA has so far been difficult to deliver systemically while maintaining activity and avoiding toxicity. Localized delivery might be more promising in averting side effects and maintaining the highest load in the target area. However, few material systems have as yet been developed to deliver siRNA in a localized and sustained manner.

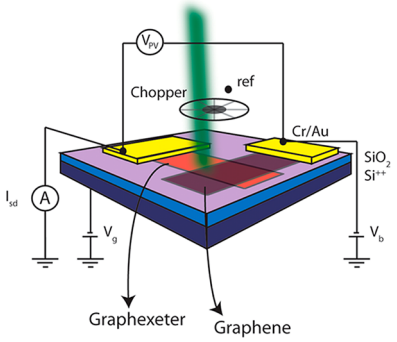
Seeking a new way to deliver siRNA locally, Castleberry *et al.* (DOI: 10.1021/nn401011n) coated siRNA onto nylon dressings often used for wound healing. For their substrate, the researchers chose Tegaderm, a woven nylon bandage that is biologically inert. The researchers tested four different coating formulations for rates of film growth, siRNA incorporation, and level of knockdown on green fluorescent protein (GFP)-expressing cells. Settling on the film with the greatest reduction in GFP expression, the most siRNA per area, and the least impact on cell viability, the researchers performed a detailed characterization. Results showed that the top film released siRNA over a 10-day period. The released siRNA was effectively taken up in GFP-expressing cells and knocked down GFP expression, even several days after the film began to degrade. Further tests showed that these effects extended to different types of siRNA to knockdown different genes in other types of cells. The authors suggest that bandages coated with siRNA-releasing films offer a promising pathway for locally administering this therapeutic molecule.



Photodetectors Go All-Graphene

The band gaps of the standard semiconductors used thus far in solar cells restrict their photoresponsivity to limited bandwidths. Research into tandem solar cells that utilize a multijunction design of stacked p−n interfaces has shown that these solar cells can successfully harvest energy from light over a broader spectrum. However, these devices are typically heavy and brittle, making them unsuitable for use in flexible electronic devices. One solution to these problems is using single- or few-layer graphene, which has no band gap and is also ultra-lightweight, flexible, and optically transparent. Such all-graphene devices, with their active areas and electrodes consisting of graphene materials, have not yet been developed.

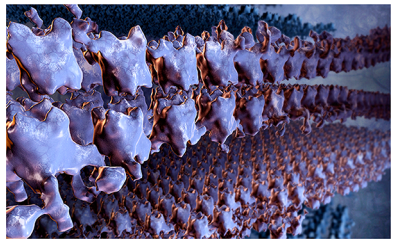
In a step closer to this goal, Withers *et al.* (DOI: 10.1021/nn4005704) developed a novel photodetector composed of pristine graphene and few-layer graphene intercalated with $FeCl_3$ ($FeCl_3$−FLG). The researchers constructed this device by depositing pristine few-layer graphene onto a Si/SiO_2 substrate, then intercalating this graphene with $FeCl_3$ to make it heavily p-doped. A pristine few-layer graphene flake was deposited on top. The researchers then attached multiple Cr/Au electrical contacts to both layers to characterize this device. Tests showed that prominent photovoltage signals were generated at the graphene/$FeCl_3$−FLG and graphene/Au interfaces. Only a negligible photovoltage originated at the $FeCl_3$−FLG/Au interface. Upon sweeping the chemical potential of the graphene layer through the charge neutrality point, the researchers found that the sign of the photovoltage changed, which they attribute to the photothermoelectric effect. The authors suggest that their results provide a better understanding of graphene-based heterostructures, a first step toward all-graphene-based photodetectors and photovoltaics.



Layering on the Proteins

Many bacteria and archea have a two-dimensional (2D) crystalline lattice of S-layer proteins (SbpA) on their surfaces. These proteins have highly regular nanoscale features and can be easily reproduced *in vitro*, making them attractive for a variety of nanomaterials engineering uses. S-layer proteins have been used in several different 2D applications, such as templates to deposit nanoparticles on surfaces or as masks for nanofabrication. Protein-based three-dimensional (3D) assemblies with ordered nanofeatures could serve as building blocks for materials with other appealing applications, such as catalysis, energy storage, and nanophotonics. However, growing stacked S-layer crystals has thus far proven to be a difficult task.

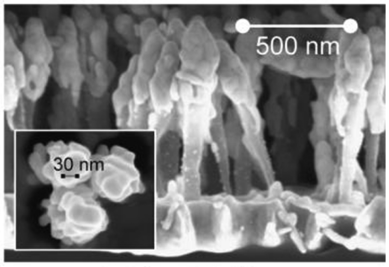
Making headway toward this objective, Shin *et al.* (DOI: 10.1021/nn400263j) report assembly of stable bilayers constructed from truncated S-layer protein. With previous research showing that the 200 C-terminal residues do not critically participate in 2D lattice structures, the researchers developed a recombinant SbpA (rSbpA) that substituted these residues with a 16-residue epitope tag. Tests show that this new protein readily forms films of 2D crystals that match the lattice parameters of wild-type SbpA. However, in thicker areas of the film, the researchers found mixtures of monolayers and bilayers. These bilayers had the same highly ordered architecture as the monolayers, with one layer displaced relative to the other. The authors suggest that the stable formation of these bilayers could make them suitable for use in hierarchical 3D assemblies. With further engineering, they add, it might be possible to achieve more extended arrays in the third dimension.



Counting Biomolecules with SERS

Surface-enhanced Raman spectroscopy (SERS) has become a popular tool for biosensing applications. This technique provides ultrahigh sensitivity through amplifying Raman signals by up to 14 orders of magnitude, and it offers the ability to identify molecules specifically based on the unique fingerprint of their Raman spectra. However, using this technique to quantify biomolecules has been hindered by poor uniformity and reproducibility of SERS-active nanostructured platforms, the lack of specific binding, and fluctuations in signal intensities. These issues must be solved in order to develop SERS-based quantitative bioassays.

Seeking to revamp SERS for quantitative biosensing, Yang *et al.* (DOI: 10.1021/nn401199k) developed a new approach based on a novel SERS substrate bearing



Leaning nanopillars

Au-decorated Si nanopillars. These nanopillars were functionalized with vasopressin aptamers for specific binding of the biomolecules vasopressin. After aptamer functionalization, the researchers applied a monolayer of 6-mercapto-1-hexanol spacer molecules to prevent nonspecific adsorption of the target molecules and to improve the aptamer's capturing efficiency. After these substrates were incubated with TAMRA (5-carboxytetramethylrhodamine) labeled vasopressin, they were washed with buffer solution and water, then allowed to dry. Surface tension during drying caused nanopillars to lean toward each other, forming clusters that result in near-field coupling effects. Using both TAMRA vibrational peaks, tests showed that SERS could successfully quantify captured vasopressin, with higher analyte concentrations causing more abundant and brighter hotspots. The researchers developed an analytical model to predict hotspot intensities for molecular quantification, showing that their method could detect molecules in the picometer range. The authors suggest that this technique could be a promising way to quantify low-abundance biomolecules.