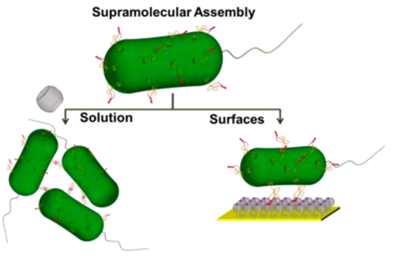
It is Alive! Bacteria Join Supramolecular Monolayers

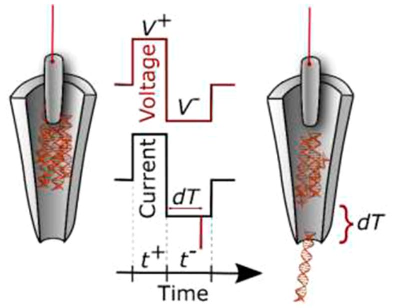
Most complex cellular processes in nature happen through dynamic, noncovalent interactions between individual molecules or molecular assemblies. These include bacterial behavior such as chemotaxis, quorum sensing, surface adhesion, and biofilm formation. Many research groups have sought to mimic these interactions through development of self-assembly-based responsive supramolecular materials with applications such as bacterial detection, antimicrobial therapies, and bacterial biomotor systems. Improving on this strategy, a few recent innovative studies have tailored supramolecular building blocks directly into the membranes of living cells.

Combining these two capabilities, Sankaran *et al.* (DOI: 10.1021/acsnano.5b00694) developed a strategy allowing bacteria to express miniproteins on their surfaces that bound to a host protein that could be incorporated into self-assembled monolayers, making living cells components of these structures. The researchers engineered *Escherichia coli* that expressed miniproteins on their surfaces with specific peptide sequences that bind to curcurbit[8]uril (CB[8]), a host molecule in a family already used in developing constructs and platforms for biosensing and manipulating living cells. Tests showed that, in the presence of CB[8], bacteria displaying these miniproteins quickly aggregated with rates dependent on both CB[8] concentration and bacterial densities. By creating monolayers with built-in CB[8] on gold substrates, the researchers were able to immobilize these bacteria onto surfaces. Although these bacteria were surface-bound, microscopy showed that they retained their motility for up to 4 h. Additionally, by introducing a CB[8]-binding peptide, the researchers reversed this binding, allowing the bacteria to detach rapidly. The authors suggest that these techniques could be easily modified to apply to other bacterial strains and different host molecules.



Tiny Pipettes Deliver DNA

Nanotechnology research has often focused on rapid single-molecule detection and controllable single-molecule delivery. However, these two areas have rarely been combined, particularly for applications requiring physiological and label-free conditions. For example, although nanopores have shown exceptional potential for analyzing DNA, RNA, and proteins, they have yet to be used for controlled delivery of these biomolecular species. Nanopipettes, a subclass of nanopores that consist of sharp tips with a single nanopore, have primarily been used to detect single molecules by transporting them from the outside reservoir to the nanopipette's inside, rather than as single-molecule delivery vehicles.

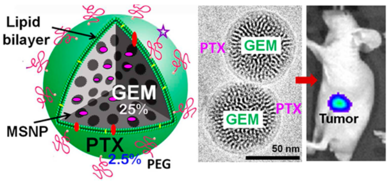


Seeking to address this gap, Ivanov *et al.* (DOI: 10.1021/acsnano.5b00911) demonstrated that quartz nanopipettes could be used to deliver single DNA molecules with precise timing from solutions with picometer concentrations. The researchers fitted nanopipettes filled with solutions of either 5 or 10 kbp double-stranded DNA with Ag/AgCl electrodes both inside the nanopipettes and in the external reservoir containing only buffer. By applying periodic pulses of positive and negative potentials, the researchers showed that they could control the number of DNA molecules translocated through the tip by varying the magnitudes and durations of these pulses. By carefully tailoring these variables, they demonstrated the delivery of individual DNA molecules from solutions with concentrations as low as 3 pM. The authors suggest a wide range of applications, including targeted delivery of nucleic acids, gene regulation, infection, and single-molecule PCR.

One-Two Punch for Pancreatic Cancer

Pancreatic ductal adenocarcinoma has a mean survival rate of mere months, and its 5 year survival rate has remained unchanged despite significant advances for other major cancers. One reason for this poor prognosis is this cancer's typical resistance to chemotherapeutic agents, including gemcitabine (GEM), often used as a first-line therapy. Although this resistance can arise through the acquired or intrinsic pathways that other cancers develop to chemotherapy, it also results from a dense, dysplastic stroma that acts as a barrier for tumor access as well as GEM pharmacokinetics that lead to insufficient activation or rapid inactivation. Drug delivery by nanocarriers could significantly address these issues. For example, Abraxane, a recently FDA-approved nanocarrier for chemotherapeutic agent paclitaxel (PTX), acts as both a stromal targeting agent that can also increase the effectiveness of GEM and has shown promise in extending survival. However, like most therapeutic nanocarriers developed thus far, this drug is a monocarrier.

Hoping to improve on the potential of this therapy, Meng *et al.* (DOI: 10.1021/acsnano.5b00510) developed a mesoporous silica nanoparticle platform that combines GEM and PTX. The researchers soaked the nanoparticles in solutions containing GEM, then encapsulated PTX inside underneath a lipid coating using a ratio of the two drugs with the highest synergy in treating pancreatic cancer cells. Tests *in vitro* and in xenograft and orthotopic models show that these two-drug carriers killed cancer cells, shrunk tumors, inhibited tumor growth, and eliminated metastasis significantly better than carriers with just GEM, free GEM, or free GEM plus Abraxane. The authors suggest that this system could hold significant promise in advancing pancreatic cancer treatment.



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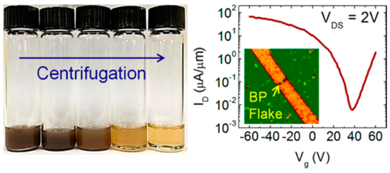
Solvent Exfoliation for Phosphorus Gets in the Black

The extraordinary electronic properties of black phosphorus (BP), including semiconduction, a customizable band gap, and high on/off ratios and room-temperature mobilities, have made this material a contender to other two-dimensional (2D) nanomaterials frequently used for electronic applications, including graphene and transition metal dichalcogenides. This layered, anisotropic allotrope of phosphorus has several production methods, including micromechanical exfoliation, chemical vapor deposition, chemical exfoliation, and liquid-phase exfoliation. However, each of these methods has had some drawbacks, ranging from lack of scalability to introducing defects that compromise electronic capabilities. Additionally, recent reports suggest that mechanically exfoliated 2D BP flakes irreversibly degrade to oxidized phosphorus compounds with ambient exposure.

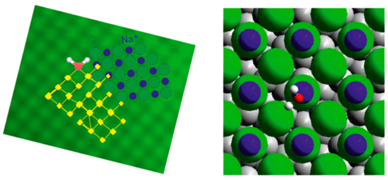
Seeking a new way to produce 2D BP without these drawbacks, Kang *et al.* (DOI: 10.1021/acsnano.5b01143) used an ultrasonificaiton system to exfoliate this material from bulk BP crystals in an organic solvent. The researchers found their ideal solvent in *N*-methylpyrrolidone (NMP), whose high boiling point and surface tension effectively increased exfoliation but also coated the resulting nanoflakes to slow oxidative degradation. Several analytical techniques confirmed the high chemical quality of the exfoliated BP nanosheets. Additionally, when they were incorporated into field-effect transistors, BP nanosheets exfoliated by this novel method showed similar properties to micromechanically exfoliated BP, suggesting that this solvent exfoliation method does not compromise electrical or structural qualities. The authors suggest that this scalable method could bring BP nanosheets to a variety of electronic and optoelectronic applications.



Like Water for Salt

Because water is one of the most important substances in nature, understanding its kinetics at surfaces is critical for many branches of science. Researchers have long held a thorough understanding of the interactions of water with NaCl from a macroscopic thermodynamic perspective, but few experiments have attempted to elucidate this interaction on the microscopic scale. For example, current knowledge of the diffusion of individual water molecules on NaCl molecules is based on density functional theory calculations rather than experiments.

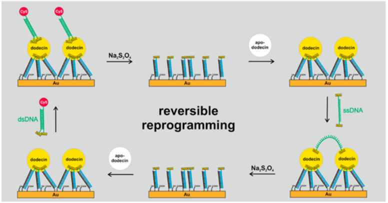
In a new study, Heidorn *et al.* (DOI: 10.1021/acsnano.5b00691) present some of the first experimental findings of water diffusion on NaCl(100) at the single-molecule level. To investigate this phenomenon, the researchers used scanning tunneling microscopy to look at the diffusion of D_2O on bilayer NaCl islands on an Ag(111) surface at temperatures between 42.3 and 52.3 K. By combining theoretical calculations and experimental findings, the researchers propose a mechanism for D_2O diffusion deemed the O-flip, in which the oxygen atom of the water rotates 180° around the axis formed by its two hydrogen bonds pointing to the same Cl^- ions. Consequently, the molecule keeps only one of its hydrogen bonds to the Cl^- ion. This action combined with in-cell motions, they suggest, is responsible for water's diffusion on NaCl. Additional investigations with low-temperature adsorption site determination and density functional theory suggest that the metallic support influences the intermediate state of this diffusion. Consequently, the authors say, the thickness of the NaCl layer might influence water molecules, their diffusion, and their reaction kinetics.



Dodecin Adds New Flavor to Surfaces

Interest continues to grow in developing "smart" surfaces for nanobiotechnology with properties that can be switched with external stimuli such as pH, temperature, light, electrochemical potential, enzymatic reactions, or ligand binding. Some smart surfaces engineered thus far have relied on guest–host systems to impart desired qualities.

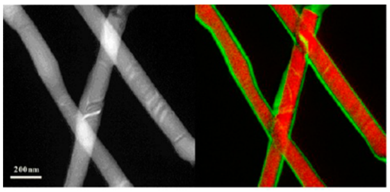
In a new study, Gutiérrez Sánchez *et al.* (DOI: 10.1021/nn506993s) developed a new way to modify surfaces using the multiligand-binding host flavoprotein dodecin. Derived from *Holobacterium salinarum*, this dodecameric hollow-spherical riboflavin-binding protein has six binding pockets, with each pocket having the capacity to bind up to two flavin ligands. Taking advantage of these properties, the researchers constructed a system in which they tethered flavins to a gold surface with DNA at various levels of coverage, then added apododecin molecules to bind the attached flavins. Even though a single apododecin bond is relatively weak, the researchers found that, at 100% DNA-flavin surface coverage, the apododecin molecules achieved multiple binding events, resulting in a stable monolayer of adsorbed protein that could not be rinsed off. By adding bi- or multivalent flavin ligands on top of these dodecin monolayers, the researchers were able to achieve a sandwich-like architecture with dodecin between two layers of flavins. All of the dodecin–flavin structures proved fully reversible, detaching when the researchers added flavin reducers to the mix. The authors suggest that this reversible and rewritable technology that relies on dodecin and tethered flavins could play an important role for a variety of applications in nanobiotechnology.



Graphite Does the Splits for Lithium Ion Batteries

■ Ge has been considered as a potential alternative to graphite as the anode material for lithium ion batteries because of its excellent lithium diffusivity and high theoretical capacity of 1600 mAh/g, which ranks second only to Si. However, this theoretical capacity has never been reached due to bad rate performance from extreme expansion during lithiation that can more than triple this material's volume, which eventually pulverizes the anode. Researchers have explored various ways to overcome this issue, including combining Ge with various forms of carbon. Reports have indicated some success with Ge micro-nanoparticles or nanowires covered with amorphous carbon. However, fabricating high-quality Ge–C one-dimensional noncables in a simple and scalable way remains a challenge.

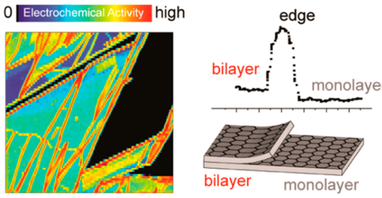
Toward this end, Sun *et al.* (DOI: 10.1021/nn506955f) report Ge nanowires-in-graphite tubes fabricated with a simple, one-step chemical vapor deposition process. Using GeO_2 and CH_4 as starting materials, the researchers produced nanowires with a Ge core wrapped by a graphite shell with a thickness of about 20 nm. Testing the performance of this material in half cells, the researchers found that the graphite not only facilitated lithium ion and electron transport but also exhibited highly stable performance up to 100 cycles. Further investigation showed that, upon charging, the graphite layer split with either inside-out or outside-in effect, resulting from either a solid electrolyte interface layer growing along the Ge–graphite interface or the lateral diffusion of lithium ions across the shell. Afterward, the Ge core and graphite remained in close contact. The authors suggest that this composite could contribute to the design of improved anodes for lithium ion batteries.



Living on the Edge for Graphene and Highly Oriented Pyrolytic Graphite

■ The extraordinary promise that graphene shows in a variety for applications, including next generation electronic, optical, mechanical, and chemical devices, might be further enhanced by effects contributed by the edges of this material. A bevy of studies have shown that the edges, which can have either armchair or zigzag terminations, can significantly affect the electronic band structure, with armchair and zigzag edges displaying different electronic states, scattering properties, and chemical features. Although graphene's electrochemistry has attracted growing interest for applications in energy and edge functionalization, researchers still know little about the electrochemistry of step edges for graphene or graphite.

In a new study, Güell *et al.* (DOI: 10.1021/acsnano.5b00550) studied the basal surfaces and step edges of graphene and highly oriented pyrolytic graphite (HOPG) using $Ru(NH_3)_6^{3+/2+}$, a redox probe whose standard potential lies near the intrinsic Fermi level of graphene and graphite. Using scanning electrochemical cell microscopy and other complementary microscopy techniques, including atomic force microscopy and micro-Raman, the researchers found a strong dependence of the electron transfer kinetics on the number of graphene layers, with rates increasing with layer number. In graphene and HOPG that were analyzed at similar time points after cleavage, there were distinct differences in the electrochemical activity between basal planes and step edges. These differences were accentuated over time in HOPG. The authors suggest that these findings could lead to better understanding of both materials, which could eventually advance their use in a variety of applications.



Better Catalysts: Not Just a Phase

■ Synergistic effects often play an important role in catalysis, with multiple active components contributing effects that lead to greater results than the total of the individual components acting alone. Finding ways to exploit this effect by controlling catalyst structure at active sites both at the atomic scale and mesoscale could help optimize catalyzation. However, attaining this level of control can be difficult for materials that are structurally complicated and have multiple active phases, such as molybdenum–vanadium-based complex oxide catalysts (Mo–V–M–O, where M = Ta, Nb, Sb, or Te). These materials have two phases, M1 and M2, that are structurally different and typically mixed in most compositions. Better understanding of the contributions of these phases could help improve catalysis for propane ammoxidation reactions to make acrylonitrile, an industrially important chemical produced at a scale of 6 million tons annually.

In a new study, He *et al.* (DOI: 10.1021/acsnano.5b00271) used aberration-corrected scanning transmission electron microscopy to gain better insight into the mesoscale structure of these materials. This technique shows that, in a Mo–V–Te–Ta oxide catalyst, the interior of particles is the M2 phase, but the surfaces of these particles are decorated with a distinct layer of M1 units. Further investigation suggests that formation of these M1 units appears to depend on Ta in the precursor solution. By enhancing intergrowth of these epitaxial phases, the researchers show improved catalytic activity for propane ammoxidation reactions compared to catalysts composed of just M1 or M2. The authors suggest that the activity of other complex catalytic systems might also benefit from similar analysis and tweaks in conformation.