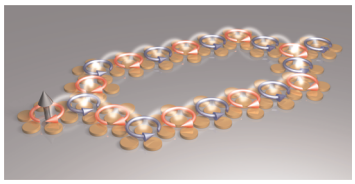
Doing, and Propagating, the Wave

Metallic nanostructures' ability to propagate plasmons between particles makes these materials potentially promising components for semiconductor-based large-scale integrated circuits. Because micrometer-scale plasmonic structures are not subject to the free-space diffraction limit of light, they open possibilities beyond those currently available. For these components to reach their potential, researchers must develop ways to guide plasmonic waves in desired directions. Although some research has shown that plasmonic waveguides composed of gold nanoparticles in linear chains can successfully propagate subwavelength plasmons, energy decay restricts the chain lengths to only a few hundred nanometers.

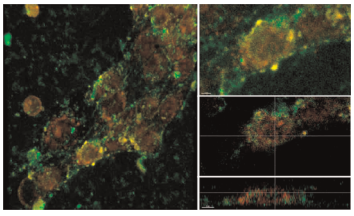
Seeking a solution for longer propagation, Liu *et al.* (DOI: 10.1021/nn301393x) developed clusters of nanoparticles that mimic the spatial geometries of the organic molecules chrysene and triphenylene. After fabricating these nanosize gold structures using electron beam lithography, the researchers arranged them in chains and used experiments and simulations to determine their ability to propagate and to guide plasmonic waves. Results showed that the chrysene analogue effectively steered waves over large-angle bends with a decay length of 2.2 μm, far longer than the 410 nm shown in recent experiments using a propagation system composed of gold nanorods. Using the triphenylene analogues, the researchers showed that plasmonic waves could be split at Y-shaped intersections, then brought together for further propagation. Further experiments showed that varying the number of units in branches of the Y could be used to create a Mach–Zehnder interferometer. The authors suggest that these systems could eventually be used for information processing and data storage applications.



To Predict a Drug's Success, Look to the Nucleus

Cancer chemotherapeutics often have severe drawbacks that limit their use, including inadequate dosing at tumor sites, short- and long-term drug toxicity, and tumor recurrence due to drug resistance. Recent research suggests that using nanomaterials as drug delivery vehicles can avoid some of these problems. However, these nanoformulations have not provided a treatment advantage to some drugs, such as cisplatin and doxorubicin, which kill cancer cells by intercalating into DNA. To determine whether new nanoformulations of these drugs can effectively hit their targets, a way to image the cell nucleus effectively during treatment is needed.

Making progress toward that goal, Bhirde *et al.* (DOI: 10.1021/nn300516g) developed a new nanoformulation that combined doxorubicin with superparamagnetic iron oxide nanoparticles (SPIONPs), a material previously developed for MRI contrast agents and as magnetic labels for tracking stem cells. Although this combination has been shown to reach tumor sites effectively, it has not been investigated using live imaging in whole cells. To investigate, the researchers

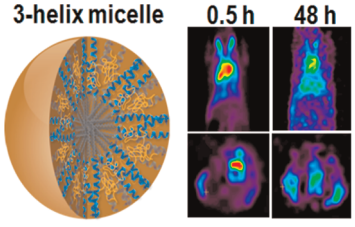


synthesized SPIONPs coated with polyethyleneimine (PEI), a biologically friendly material that shields foreign material from the immune system, and loaded them with doxorubicin. Using a new type of image analysis, the researchers were able to map these particles to the cell nucleus. Findings showed that both drug-sensitive and drug-resistant cells had significantly greater uptake of the nanoformulation than the free drug, with more of the drug-loaded nanoparticles accumulating in the perinuclear area and the drug accumulating in the nucleus. The authors suggest that their new computational model could help predict the success of drug formulations that need to reach the cell nucleus to be effective.

Micelle Drug Carriers Go the Long Haul

Nanosized drug carriers have the potential to improve cancer care through the enhanced permeation and retention effect, which allows nanoparticles to accumulate within cancerous tissue due to solid tumors' inherent leaky vasculature and poor lymphatic drainage. However, two FDA-approved drugs, Doxil and Abraxane (~100 and 130 nm, respectively), provide only modest survival benefits due to inefficient uptake into tumors. For nanosized drug carriers to be truly effective, they need to be significantly smaller, to have extended circulation *in vivo*, to minimize cargo leakage, and eventually to degrade for safe renal clearance to reduce systemic toxicity.

Taking all of these design features into consideration, Dong *et al.* (DOI: 10.1021/nn301142r) developed micelles that self-assemble from peptide helices that group together into bundles of three. Conjugating these helices to the biologically friendly material polyethylene glycol, the resulting micelles are shielded from immediate clearance by the immune system. Tests showed that these nanoparticles, only 15 nm in diameter, could carry about 8 wt % of the chemotherapeutic agent doxorubicin. Experiments using micelles loaded with Förster resonance energy transfer pairs demonstrated that the micelles were stable after 12 h in serum proteins at human body temperature. Using mouse models, these nanosized carriers showed a circulation half-life of more than a day. Additionally, the researchers found little accumulation in the liver, spleen, and intestines, suggesting that these micelles are broken down over time. The authors suggest that their micelles show potential not only as drug carriers for cancer therapeutics but also for a variety of other formulations that require distribution in this size range and extended circulation.



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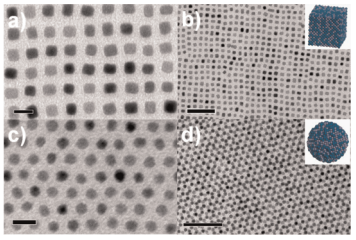
Catalysts Go Platinum, without the High Cost

■ Polymer electrolyte membrane fuel cells have been extensively investigated as potential power sources for portable devices, with liquid fuels such as small organic molecules providing energy. Of all the pure metals, Pt is the best catalyst for oxidation of these fuels. However, it is also expensive and has a low CO poisoning tolerance. To overcome these problems, researchers have sought alternative electrocatalysts that function just as efficiently as Pt. Intermetallic PtZn particles have shown significant activity toward formic acid and methanol, but so far, these materials have been synthesized only through reaction of Pt in Zn vapor and not directly as nanocrystals.

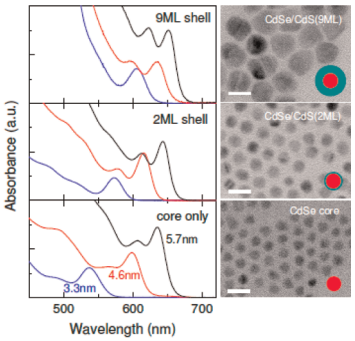
In a new study, Kang *et al.* (DOI: 10.1021/nn301583g) directly synthesized Pt_3Zn nanocrystals by mixing Pt and Zn solutions, then heating to 350 °C for up to 60 min. This method produced spherical Pt–Zn nanocrystals, while adding benzyl-ether-produced cubic ones. These nanocrystals are Pt–Zn alloys, but annealing at 600 °C for 30 min converted them to the intermetallic phase. Tests showed that the 350 °C reaction temperature was essential for producing the desired combined nanocrystals in the absence of a strong reducing agent. In a series of experiments, the researchers showed that these nanocrystals had maximum methanol electro-oxidation activity comparable to that of a commercial Pt catalyst, with the spherical nanoparticles showing higher activity than the cubic ones. Both the spherical and cubic nanoparticles showed excellent CO poisoning tolerance. The authors suggest that these materials could offer a promising solution for catalysis at a lower cost in direct methanol fuel cells.



Quantum Dots: Going through a Dephase

■ Understanding the quantum dynamics of excitons in semiconductor quantum dots (QDs) is important for fundamental knowledge as well as for applications such as quantum computing or advanced photonics devices. Most work thus far has been done with epitaxially grown QDs. However, advances in colloidal synthesis have produced high-quality semiconductor nanocrystals. While epitaxially grown QDs have shown that exciton dephasing is nonexponential even at lower temperatures, with a sharp zero-phonon line (ZPL) superimposed onto a broad acoustic phonon band, it is unclear how this process occurs in colloidal QDs, whose smaller sizes and stronger dielectric confinements lead to longer radiative lifetimes. Recent research on CdSe/ZnS wurtzite QDs suggests that ZPL dephasing at 5 K originates from rapid phonon-assisted spin-flip from the lowest bright state to the dark exciton state.

Building on these findings, Accanto *et al.* (DOI: 10.1021/nn300992a) hypothesized that the time scale of exciton dephasing might be controllable through engineering

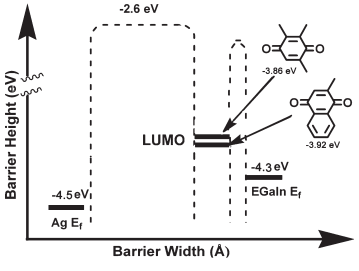


QDs with variable fine structure splitting energy. Testing this idea, they measured dephasing in a series of CdSe/CdS QDs with different core diameters and different CdS shell monolayer thicknesses. They tested each of these colloidal QDs over a range of temperatures using a sensitive three-beam four-wave-mixing photon echo technique, which is not affected by spectral diffusion. Results demonstrate that dephasing can indeed be controlled by core size and shell thickness. As the core size and shell thickness increased, the researchers found that ZPL dephasing times increased at 5 K. The authors suggest that this ability to tailor exciton dephasing time is an important step toward using colloidal QDs for quantum dynamics applications.

Rectifying a Rectification Mystery

■ Electrical junctions composed of eutectic Ga and In (EGaIn) as a top electrode and Ag as a bottom electrode, with a self-assembled monolayer containing alkanethiols and ferrocene groups between, have been reported to rectify current. However, the mechanism behind this rectification has been unclear. Although the characteristics of most components of this system are well understood, little is known about the thin film consisting primarily of Ga_2O_3 that forms when EGaIn is exposed to air. In principle, this oxide film might have substantial effects that could be responsible for the rectification effect, such as contributing resistance to the junction, having molecular effects caused by adsorbed organic contaminants, or having the potential for redox behavior or other processes that cause electrical artifacts.

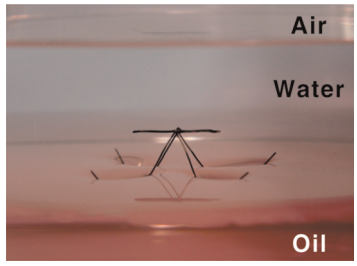
Reus *et al.* (DOI: 10.1021/nn205089u) consider an exhaustive list of potential mechanisms, from both previously published and new experiments, that might be responsible for the observed rectification in this system. They conclude that factors involving the Ga_2O_3 layer or the asymmetry of the electrodes do not explain the high rectification values. Rather, the molecular structure of the self-assembled monolayer itself is likely causing the observed rectification. Their experiments suggest that the presence of a molecular orbital located asymmetrically between the two electrodes leads to rectification. Specifically, the ferrocene group appears to provide a highest occupied molecular orbital that is slightly offset compared to the Fermi energies of both metals. The authors suggest that although their findings appear to explain rectification in this system, claims of molecular rectification in other systems need to be carefully examined on a case-by-case basis because charge transport in organic matter is not completely understood.



Oil Striders, Based on a Bug

■ Oil spills harm not only the environment but also the equipment later brought in to stop oil loss, to clean up spills, and to provide environmental remediation. To solve this problem, researchers would need to develop aquatic devices that travel freely at the interface between water and oil that are highly oil-repellant to avoid oil fouling. Thus far, teams of investigators have successfully developed a variety of superoleophobic surfaces, including one that mimics nature by using a mechanism much like that in self-cleaning fish skin. However, translating these surfaces to smart aquatic devices has not yet been explored.

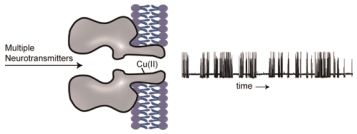
Looking to nature again, Liu *et al.* (DOI: 10.1021/nn301550v) used superoleophobic copper wires to fabricate "oil striders" based on the insects known as water striders. Using copper wires that were 280 μm in diameter, about the same as a water strider's legs, the researchers made two bends to approximate the insect's leg shape. They then immersed the wires in aqueous ammonia to generate a rough, black coating of copper oxide. Scanning electron microscopy showed that this coating was composed of flower-like microclusters of up to 5 μm in diameter, with "petals" about 100 nm in width. Tests showed that these treated wires displayed superoleophobic properties, with high contact angles in 1,2-dichloroethane oil. Shaped into a body form mimicking that of a water strider, the oil striders maintained a position on top of oil in an oil–water interface, even under the duress of waves. The authors suggest that their oil striders could represent a first step toward creating underwater oil-cleaning devices with effective oil-repellant capabilities.



Neurotransmitters Boldly Transmit Where They Have Never Transmitted Before

■ To understand how the nervous system operates, it will be necessary to assess which neurotransmitters are released from individual neurons under particular circumstances. However, multiple neurotransmitters and neuromodulators are frequently released from the same presynaptic neuron into the synaptic cleft. Researchers have yet to develop reliable techniques to distinguish among these various entities. Although carbon electrodes can be used to detect the presence of dopamine and other neurotransmitters, and fast scanning cyclic voltammetry can detect catecholamines, these techniques have drawbacks. For example, generally only one neurotransmitter can be monitored at a time, and irrelevant oxidizable compounds can give a strong background signal, muddling results.

To avoid these issues, Boersma *et al.* (DOI: 10.1021/nn301125y) turned to α-hemolysin (αHL) nanopores. Inserted into a lipid bilayer, with an ion gradient on either side, these protein nanopores have been used to detect a variety of different



analytes based on a change in potential. The researchers took advantage of this system by using chemical post-translational modification to install the heterocyclic organic compound phenanthroline, which complexes with most metal ions, on the *trans* side of the bilayer. To this molecule, they then attached a copper(II) ion, to which many neurotransmitters have a high, but reversible, affinity. Tests showed that this nanopore could reliably detect and distinguish the passage of a variety of neurotransmitters and neuromodulators, including glutamate, dopamine, epinephrine, norepinephrine, ATP, and ADP. These components could be distinguished both alone and in combination. The authors suggest that nanopores could be used to provide a time-dependent fingerprint of neurotransmitters released in response to various situations, such as applications of drugs to tissues.

Powering Up with GaN Nanowires

■ Devices with nanosized components that harvest energy, including solar cells, fuel cells, and piezoelectric systems, have gathered increasing attention in recent years. In the latter category, materials with a wurtzite structure, such as ZnO, have demonstrated some success as components for piezoelectric nanogenerators and piezotronics. GaN has the same crystal structure and similar physical properties as ZnO and could feasibly serve as the core nanostructure for light-emitting diodes (LEDs) or piezoelectric devices. However, although ZnO has been the focus of a variety of experiments in this area, relatively few have tested the suitability of using GaN for these devices.

Putting GaN nanowires to the test, Chen *et al.* (DOI: 10.1021/nn301814w) used this material as the core for a nanogenerator and an LED. Using p-type GaN-coated sapphire as a substrate, the researchers grew n-type GaN nanowires with a vapor–liquid–solid process, ending up with GaN nanowires of about 3 μm in length and 5 nm in diameter. They then used the Pt-coated Si tip of an atomic force microscope to characterize this nanogenerator's energy harvesting properties. Their results showed that this device could generate an average output voltage of 24.95 mV and average output current of 49.90 pA in an area of 100 μm^2, values that translate into a power density of about 12.5 mW/m^2. Trying this power in an LED powered by a ZnO nanogenerator, the researchers were able to keep the device lighted for about 3 s at a time. On the basis of these results, the authors suggest that GaN shows high potential for use in piezotronics and especially LEDs, which could eventually be driven by their own internal power outputs for very low power consumption in future nanotechnology applications.