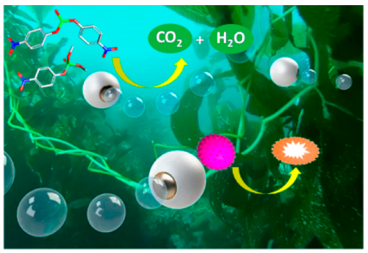
Fighting Back against Chemical and Biological Warfare

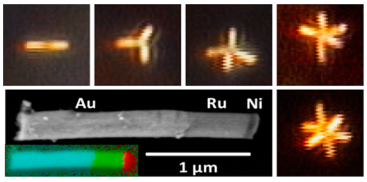
Over the past several decades, concern has steadily grown over the potential use of chemical and biological warfare agents (CBWA), including nerve agents and *Bacillus anthracis*. Although researchers have developed a promising approach for degrading these agents through photocatalysis using TiO_2, this technique has several drawbacks. For example, this method generally requires controlled agitation of TiO_2 with a contaminated solution, which can be challenging to provide in the field.

Expanding on this protocol, Li *et al.* (DOI: 10.1021/nn505029k) developed TiO_2-coated microspheres that agitate solutions of CBWA autonomously without external fuel. The researchers synthesized these microspheres by dispersing Mg particles on a glass slide and sputter-coating them first with a thin layer of Au nanoparticles. Then, using atomic layer deposition, they grew an outer coat of photoactive TiO_2. The small portion of the microspheres adjacent to the slide remained uncoated. Consequently, when placed in water, the exposed Mg reacted with chloride, leading to an oxidation reaction that caused hydrogen bubbles to form at this opening, thrusting the microspheres forward. Tests show that within 10 min, these novel particles could degrade nearly all of two nerve agents, methyl paraoxon and bis(4-nitrophenyl)phosphate, in seawater after exposure to ultraviolet light, showing their promise for large-scale degradation of toxic agents. Similarly, the reactive oxygen species generated by the microspheres' TiO_2 coating ruptured the membranes of nearly all *Bacillus globigii* spores, a surrogate species for *B. anthracis*. The authors suggest that these novel micromotors hold potential for use in defense and environmental applications.



A Sound New Method for Nanoassembly

Many research efforts are currently focused on finding ways to assemble higher order structures controllably from nanoscale building blocks and to capitalize on their properties. Many of these engineered structures are analogous to molecules, with properties that derive from their individual building blocks. These assemblies also have properties in common with atoms in crystals, offering insights into phenomena such as crystal nucleation. In parallel to studying assembled particles, researchers have also studied the collective interactions of powered microscale objects. Most of these studies have focused on structurally simple objects, with few investigations on more complex designs, such as self-assembled dimers and trimers.

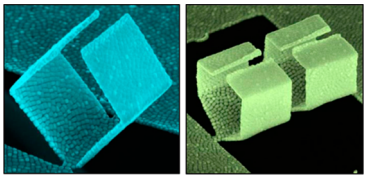


In a new study, Ahmed *et al.* (DOI: 10.1021/nn5039614) offer insight into both self-assembly and collective behavior by investigating the spontaneous assembly of magnetic nanorods into geometrically regular dimers, trimers, and higher multimers using acoustic levitation in water. The researchers fabricated Au–Ru nanorods with thin Ni segments at one end. With the application of ~4 MHz ultrasound, the rods levitated to the acoustic chamber's midplane, forming spinning chains and concentric circles of rods at the lateral acoustic nodes. Eventually, they spontaneously and dynamically assembled and disassembled into dimers, trimers, and higher multimers depending on the rod density and speed of their axial movement. Their assemblies tended to be geometrically regular, analogous to molecules. Tests showed that they could be steered within the acoustic chamber using an external magnetic field and they retained their shape when removed from water and dried. The authors suggest that these nanorod motors represent a novel example of higher-order assembly of nanoscale particles.

Giant Plasmene Nanosheets Go above the Fold

According to plasmon hybridization theory, resonance coupling can occur in well-defined plasmonic assemblies including plasmonic molecules, polymers, and two-dimensional (2D) and three-dimensional (3D) superlattices. Accordingly, free-standing plasmonic nanoparticle superlattice sheets offer a way to control hybridized plasmon modes and near-field distributions in a 2D plane, properties that in principle can be tuned by changing the sizes and shapes of the constituent nanoparticles and their interparticle spacing. Such "plasmene" nanosheets, analogous to graphene as one-particle-thick superlattices, could enable understanding of large-scale 2D self-assembly as well as practical applications in engineering flexible and stretchable plasmonic devices and circuits. However, no free-standing plasmonic nanoparticle superlattices reported thus far have been sufficiently large or capable of forming 3D plasmonic structures.

In a new study, Si *et al.* (DOI: 10.1021/nn504615a) developed plasmene nanosheets with dimensions as thin as ~40 nm and as wide as ~3 mm using bimetallic Au core/Ag shell nanocubes as building blocks. Placing droplets of polystyrene-capped nanocubes onto water drops on a holey copper grid, evaporation produced patches of monolayered nanosheets that grew together. These materials exhibited strong plasmonic resonance peaks in the extinction spectra, strong electromagnetic fields in the internanoparticle gaps, and plasmon propagation on their top surfaces. Much like graphene, these plasmene nanosheets could be milled into free-standing nanoribbons, which could in turn be folded into a variety of shapes including a cube, hexagon, heart, airplane, and an origami flying bird. The authors suggest that these materials could eventually be used for applications including flexible and stretchable plasmonics, foldable plasmonic devices, and plasmonic waveguiding.



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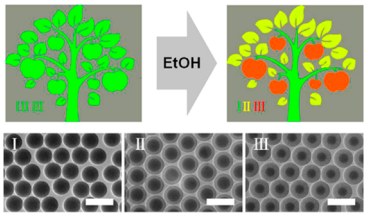
Color Shifting Ink, Inspired by a Beetle

Responsive colloidal photonic crystals' (CPCs) tunable capability to control and to manipulate light propagation has drawn great attention to these materials, with promise for applications in displays, sensors, lasers, and anti-counterfeiting trademarks. However, being able to bring many of these applications to fruition relies on finding ways to pattern them at high resolution. Researchers have developed a variety of ways to achieve this feat, but being able to pattern responsive CPCs with distinct color-shifting properties quickly, easily, and affordably remains a challenge.

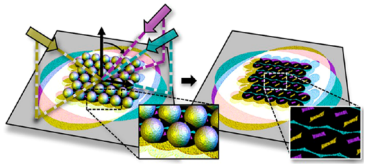
In a new study, Bai *et al.* (DOI: 10.1021/nn504659p) offer a new solution using technology inspired by nature. Looking to *Tmesisternus isabellae*, a longhorn beetle that can reversibly change color from gold to red with differences in humidity, the researchers developed ink that also shifts color when exposed to various vapors. They synthesized this ink from silica nanoparticles with mesoporous shells or solid silica nanoparticles in latex, which they inkjet printed onto solid or flexible substrates in designed patterns. On exposure to N_2, the inks maintained the same color. But when exposed to EtOH, the mesoporous particles displayed an obvious color change due to capillary condensation of vapor in their pores, leading to a change in their refractive index. By altering the thickness of the mesoporous shell or the number of pores, the researchers were able to tune this color shift, allowing them to construct images with multicolor patterns evident upon exposure to EtOH. The authors suggest that this technology holds great promise for advanced, responsive CPC applications such as anti-counterfeiting devices, multifunctional microchips, sensor arrays, or dynamic displays.



On-the-Ball Engineering for Optical Metasurfaces

Plasmonic metasurfaces—optically thin, nanostructured composites that enable precise manipulation of light—have wide-reaching applications ranging from tunable and nonlinear optics to superresolution imaging to light concentration for efficient solar harvesting and photodetection, among others. However, the ability to integrate these materials into devices as well as to understand their operation at a fundamental level has been hindered by the difficulty of fabricating the intricate, finely featured arrays of plasmonic nanoantennaes that they require. The only fabrication strategies that permit some control over arrays use conventional photo-, electron-, or ion-beam lithography. However, these processes are too expensive, slow, and limited in their ability to handle multiple materials. An alternative for creating periodic patterns is to use monolayer colloidal crystal (MCC) spheres as stencils. However, this method, known as nanosphere lithography (NSL) has only been demonstrated in a small set of simple patterns and thus remained incompatible with the broad design requirements of metasurfaces.

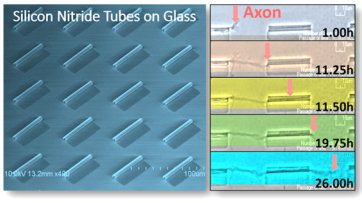
In a new study, Nemiroski *et al.* (DOI: 10.1021/nn504214b) demonstrate a variation of NSL that uses plasma-etched microspheres to engineer shadows, allowing sequential deposition from multiple angles guided by custom software. Using this technique, which they named shadow-sphere lithography (SSL), the researchers produced surfaces with many of the most common morphologies of nanoantennae, including angled resonators, chiral resonators and split dipoles. They also explored this technique as a way to discover new nano-optical patterns. The authors suggest that SSL offers a new way to prototype efficiently and to discover periodic metasurfaces.



Neural Outgrowth Goes Totally Tubular

Interest continues to grow in neural electrode interfaces, technologies that have already had an enormous impact on understanding brain cognition, implementing neuroprosthetics, and treating neural degenerative diseases. Toward improving these devices, researchers have strived to build better neural culturing platforms and more efficient electronic devices. However, integrating these systems on the same substrates and interfaces still remains a challenge. Currently, substrates for neuron culture, often bulk metal and organic semiconductors, tend to have low biocompliance and poor optical properties. These systems also often lack a means to guide growth, leading to poor fidelity of the device over time.

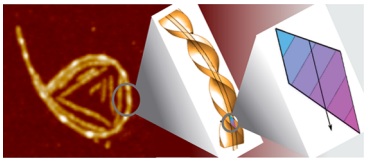
Seeking a way around these problems, Froeter *et al.* (DOI: 10.1021/nn504876y) developed a novel culturing system that uses strain-induced self-rolled-up silicon nitride (SiN_x) microtubes on a transparent substrate



to guide neuron growth and to provide access for visualization or photonics. When these microtubes were formed on a German glass coverslip, with diameter just slightly larger than that of an axon, the researchers seeded the surface with primary cortical neurons. Within hours and days, the neurons preferentially grew axons into the tubes, with some cells' outgrowth following the tubes' outer walls. This growth pattern persisted even for setups where there were large spaces between the tubes. Live cell imaging showed that as the cells extended their projections, growth sped up by as much as 20-fold as they entered the tubes, a possible consequence of confinement and the inability to branch. The authors suggest that this system could bring complex and intelligent synthetic neural circuits within reach.

Amyloid Fibrils Put a Ring on It

Amyloid fibrils are linear supramolecular protein/peptide assemblies with remarkable structural homogeneity despite a large diversity in possible peptide sequences. Peptides that compose these materials assemble into stacked β sheets that form often chiral filaments with main axes perpendicular to the β strands. These fibrils usually join into multiple filaments twisted into ribbons. Amyloid fibrils were first studied for their role in multiple degenerative diseases, including Alzheimer's, Parkinson's, and type II diabetes. However, researchers have recently explored other avenues of amyloid fibril study, including their use in materials applications and as important players in normal biological processes including hormone storage. Consequently, interest



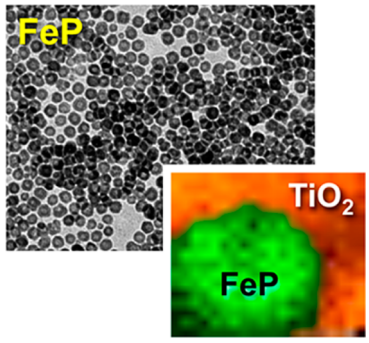
has surged in better understanding their structure and properties in two dimensions.

Toward that end, Jordens *et al.* (DOI: 10.1021/nn504249x) explored conformational changes that β-lactoglobulin fibrils undergo on adsorption to liquid−liquid or liquid−air interfaces. Atomic force microscopy, cryogenic scanning electron microscopy, and passive probe particle tracking all show that many of the fibrils at this interface passively form open rings. Calculations suggest that this spontaneous curvature occurs to minimize surface energy. By testing fibrils from different prepared batches, the researchers found that the propensity to bend into these long-lived rings was influenced by fibrillar diameter, with single- or double-stranded fibrils more likely to curve than triple-stranded fibrils. The authors suggest that these results might lead to better understanding of fibrils *in vivo* and better controlled design, fabrication, or improvement of devices that use these materials.

An Iron-Clad Solution to Electro- and Photocatalysis

Researchers typically look to Pt as the catalytic agent for the electrocatalytic and photocatalytic production of molecular hydrogen from water through the hydrogen-evolution reaction (HER), a process central to several clean energy technologies. The popularity of Pt stems from its high catalytic activity and stability under electrolyzers' and photoelectrochemical cells' harsh operational conditions. However, this material is expensive and scarce. Several other catalysts have been tested as alternatives, including MoS_2, Ni-MO, $CoSe_2$, and CoS_2. An even more attractive alternative would be an Fe-based catalyst, since this element is both widely available and significantly cheaper than other abundant and catalytically relevant metals. Although some Fe-based heterogeneous catalysts have shown moderate activity for HER, including porous FEP nanosheets, pyrrhotite-type FeS nanoparticles, and polycrystalline films of pyrite-type FeS_2, highly active Fe-based nanoparticles for this purpose have not yet been identified.

In a new study, Callejas *et al.* (DOI: 10.1021/nn5048553) find that FeP nanoparticles show exceptional activity in both electrocatalysis and photocatalysis for HER. Attaching these nanoparticles to Ti substrates, the researchers tested their electrocatalytic potential in both acidic and neutral solutions at a current density of -10 mA cm^{-2}. They found overpotentials of -50 mV in H_2SO_2, and -102 mV in phosphate buffered saline, values approaching those of Pt electrodes. The amount of H_2 collected was consistent with the charge passed through the system, indicating a faradaic yield. The FeP nanoparticles also served as effective photocatalysts, generating hydrogen in both acidic and neutral solutions under UV illumination. The authors suggest that FeP nanoparticles hold promise as cheap, abundant catalysts for HER.



This Little Light of Mine

Semiconducting films' strong light absorption and high-efficiency emission make these materials useful as components in solid-state dye lasers. The dye molecules' broad gain spectrum enables tunable lasing, and lasers made with these materials have shown the ability to deliver high pulse energies with narrow bandwidths. These dyes have been used in lasers with distributed Bragg reflectors, distributed feedback structures, whispering gallery resonators, and other designs. However, researchers have yet to demonstrate an electrically pumped organic laser. The major challenge to achieving this feat is singlet−triplet annihilation, which leads to infeasible threshold current densities. One way around this problem is lowering the threshold by controlling the laser's optical properties, including quality factor/mode volume and/or the spontaneous emission factor.

In a new study, Deotare *et al.* (DOI: 10.1021/nn504444g) combat these issues by developing an ultracompact, low-threshold organic laser using a photonic crystal nanobeam cavity (PCNC). The researchers' novel laser uses a host−guest system consisting of a tris-(8-hydroxyquinolinato)aluminum (Alq_3) film doped with 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyril)-4*H*-pyran (DCM) laser dye applied to a suspended PCNC. They pumped the Alq_3 molecules to an excited state using a 400 nm wavelength excitation laser pulse, and the energy from these excited molecules passed to nearby DCM molecules through Förster resonant energy transfer. Lasing from this device had a threshold of 4.2 $\mu J/cm^2$. The authors suggest that these devices, thus far the smallest organic lasers to be reported, have potential for use in a variety of applications including highly sensitive motion and chemosensors.