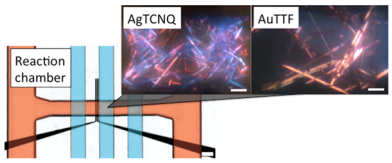
Come Together, Right Now, Over Microfluidics

Assembling complex, functionalized nanostructures often requires precise assembly pathways that allow individual molecular units to come together in orderly and reproducible ways. This organized assembly is especially important in the case of crystalline materials, whose molecular organization has enormous impact on functionality. Although defect-free molecular order has been shown to improve the performance of crystals and films greatly, and consequently the devices in which they are used, it can be difficult to enact the conditions necessary to reach this result reproducibly.

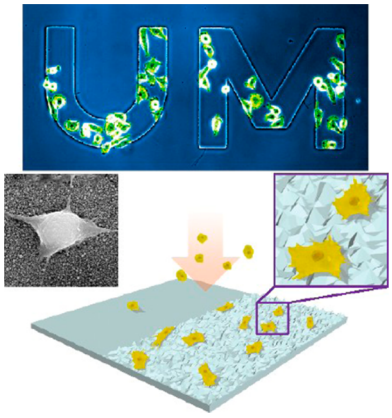
In a new study, Cvetkovic *et al.* (DOI: 10.1021/nn303632n) outline a novel method that combines such precise synthesis with characterization and utilization of nanosized materials using microfluidics. The researchers fabricated a two-layer microchip-based device with a bottom layer for fluid supply and a top layer for pneumatic actuation of a set of integrated valves. To create the desired product, two reagents enter from either side of the microchip into the microchambers while the central valve remains closed. Opening the outside valves on both sides compartmentalizes the reagents into a precise volume. When the middle valve is open, the reagents come into contact, allowing the synthesis reaction to proceed. As proof of principle, the researchers used their device to synthesize various metal–organic compounds, including silver 7,7,8,8-tetracyanoquinodimethane (AgTCNQ) crystals and crystalline gold tetrathiafulvalene (AuTTF) wires. By sealing the microfluidic device to a glass plate patterned with electrodes, the scientists were able to characterize both materials and test the AuTTF wires as a humidity sensor. The authors suggest that this approach could be useful in a variety of disciplines including molecular electronics, sensors, and optics.



Capturing Tumor Cells in the Rough

Researchers have long known that both primary and metastatic tumors shed cells into the bloodstream. These circulating tumor cells (CTCs) are thought to contribute to the spread of cancer to distant sites. Over the past several years, researchers have become increasingly interested in using CTCs as a way to predict patients' responses to therapy or overall survival. For example, studies have shown that elevated CTC levels are correlated with worse prognoses for patients with some forms of cancer, including those with metastases of breast, prostate, lung, and colon primary tumors. However, molecular and cellular understanding of CTCs remains poor, mainly because these cells have proven difficult to isolate and to purify. Most current methods require complex techniques and expensive equipment, and many require the use of capture antibodies or depend on differences in cell size, which can limit the yields of tumor cells captured.

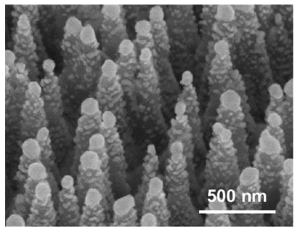
Seeking a new way to isolate CTCs, Chen *et al.* (DOI: 10.1021/nn304719q) capitalized on the different adhesion between these cells and normal blood cells to nanoroughened surfaces. Using a combination of reactive ion etching and photolithography, the researchers created nanorough areas on glass surfaces. By seeding various types of cancer cells on both the roughened and smooth glass surfaces, both alone and with a background of normal blood cells, the researchers show that the CTCs have a significantly higher propensity to attach to the nanoroughened surfaces. The authors suggest that this method could eventually lead to effective, low-cost methods to isolate CTCs from patients' bloodstreams without relying on the cells' physical sizes or capture antibodies.



Nanoribbons on the Edge

The edges of the two-dimensional sheets of carbon known as graphene have unique features, such as localized edge states, that have been theorized to play an important role in controlling this material's electronic properties. This edge-dependent behavior is thought to be especially pronounced in the ultranarrow strips of graphene known as nanoribbons, since edges make up such a high portion of their volume. Consequently, nanoribbons have the potential to open up new opportunities for novel electronic and magnetic nanodevices, but only if researchers can develop ways both to control and to correlate their edge electronic structures with chemically defined terminal edge groups.

In a step toward this goal, Zhang *et al.* (DOI: 10.1021/nn303730v) have developed a way to engineer the edges of graphene nanoribbons with hydrogen plasma etching. Using



scanning tunneling microscopy, the researchers found that treating chemically unzipped carbon nanotubes with hydrogen plasma has two prominent effects on the resulting nanoribbons' edges: it effectively removes the original edge groups and replaces them with hydrogen, while also making the edges significantly rougher and developing short segments with different chiralities along the edges of the same nanoribbon. Combining their microscopy studies with first-principles calculations, the researchers determined the exact atomic structures and the chemical nature of terminating functional groups for zigzag, armchair, and chiral edges of graphene nanoribbons. Results showed that the hydrogen plasma-treated nanoribbon edges were flat and had no structural reconstructions. Additionally, findings for the zigzag and chiral edges suggested the presence of edge states. The authors suggest that this method could eventually play a key role in engineering graphene nanoribbons to manipulate their electronic properties.

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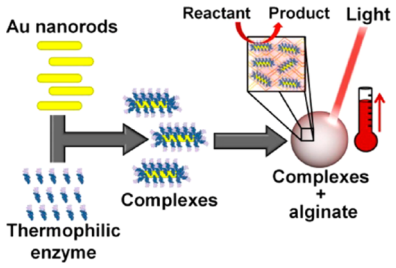
Heating Up Biocatalysis with Au Nanoparticles

Au nanoparticles have attracted significant attention for a variety of biological applications, including drug and oligonucleotide delivery, bioimaging, gene therapy, and photothermal therapy. Although these materials tend to have interesting optical properties, Au nanorods, in particular, display surface plasmon-derived effects, with collective electronic oscillations that readily and efficiently convert optical energy to thermal energy upon resonant optical illumination. This response is tunable such that Au nanorods can be designed to absorb light in the near-infrared region in which biological reactions and cells are maximally transparent, such that light can penetrate deep within tissues.

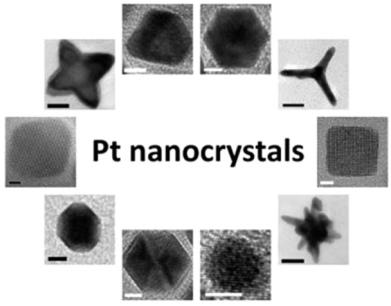
Taking advantage of this effect for a new biological application, Blankschien *et al.* (DOI: 10.1021/nn3048445) used the heat generated by Au nanorods to improve the efficiency of an enzymatic reaction. The researchers chose the model enzyme *Aeropyrum pernix* glucokinase (Glk), a key enzyme involved in sugar degradation *via* the glycolysis pathway in bacteria and eukaryotes, to demonstrate Au nanorods' influence. Linking this enzyme to the nanorods through gold–thiol chemistry and encapsulating them inside a calcium alginate matrix, the researchers illuminated the resulting combined material with a standard continuous wave near-infrared laser. This led to a significant temperature differential of about 20 °C between this material and the bulk solution. The increase in temperature boosted enzymatic activity by about 60% compared to bulk temperature controls. The authors suggest that this system could be used for a variety of useful biological effects, including improving the efficiency of PCR and the industrial manufacture of biofuels, as well as controlling whole systems by conjugating Au nanorods to enzymes that act as master regulators.



Metal Carbonyls: A Game- and Shape-Changer for Pt Nanocrystals

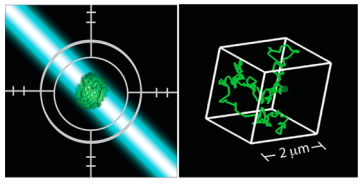
The ability to control the sizes and shapes of synthesized nanocrystals is pivotal for a variety of applications that depend on nanocrystal surface structure, including optics, magnetics, and electronics. In particular, many previous research efforts have focused on the role of shape in Pt nanocrystals for catalysis. Having well-controlled methods for synthesizing nanocrystals of predictable shape and size is pivotal for better understanding how structure affects catalytic properties. While researchers have been able to control shape at scales of tens to hundreds of nanometers for many other types of nanocrystals, synthesizing well-controlled Pt nanocrystals under 20 nm remains a challenge.

Building on previous efforts using metal carbonyls as shape-changing elements in Pt nanocrystal synthesis, Kang *et al.* (DOI: 10.1021/nn3048439) experimented with methods to create Pt nanocrystals that rely on various solvents in which metal carbonyls, particularly $Mn_2(CO)_{10}$, are dissolved prior to injection. The researchers found that using a solution of chloroform and $Mn_2(CO)_{10}$ with a 1/5 atomic ratio of Mn/Pt predictably resulted in octahedra, while varying the temperature resulted in icosahedra. The size of these latter particles was tunable through the use of other metal carbonyls, which changed the reaction rate. By using CO as a reducing agent, the researchers were able to synthesize Pt nanocubes. Changing the Mn/Pt ratio resulted in a variety of other morphologies, including cuboctahedra, near-spherical nanocrystals, star-like octapods, and multipods. The researchers suggest that this new understanding of shape control in Pt nanocrystals will be advantageous for future catalyst studies.



Block Copolymer Membranes Keep `Em Separated

Because the conventional resin-based chromatography methods used to separate mixtures of biological molecules can be time-consuming and expensive, researchers are increasingly turning to alternative separation processes that depend on membranes. These newly developed methods offer substantial economic, environmental, and safety advantages. Nanostructured membranes, in particular, have been shown to have great potential for bioseparation applications in which proteins have significantly different molecular sizes. However, current commercially available ultrafiltration membranes cannot separate similarly sized proteins. Efforts to generate new membranes with this capacity have only been partially successful, with limitations including scalability, complicated procedures, and low pore density.

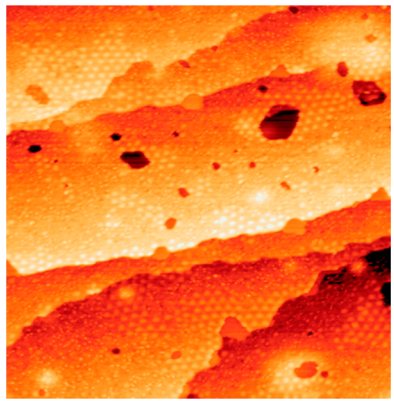


Seeking a better method for bioseparations, Qiu *et al.* (DOI: 10.1021/nn305073e) developed a nanoporous membrane using the amphiphilic block copolymer poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP). By combining the self-assembly of this material with nonsolvent-induced phase separation, the researchers synthesized an asymmetric membrane. One side of the membrane contained very dense, highly ordered cylindrical channels with uniform pore sizes perpendicular to the surface, and on the other side was a nonuniform, spongy layer. The average cylinder length was only 100 nm, which allowed high water flux. Tests with bovine serum albumin (BSA) and globulin-γ, two proteins that are too close in size to be separated by conventional dialysis membrane processes, showed that the new membrane prevented the diffusion of globulin-γ more than BSA by a factor of 87. Further experiments showed that the membrane was pH and charge responsive, selectively blocking two similarly sized, but differently charged, proteins at different pH values. The authors suggest that this novel membrane could have applications in bioscience, biotechnology, and biomedicine.

Graphene Formation: The Hole Story

A prominent challenge for synthesizing graphene on metals through epitaxial growth is avoiding high defect concentrations, particularly at boundaries between rotational domains. One way around this conundrum is growing single, large crystals of graphene to cover entire metal wafers. Researchers have had some success with this endeavor on Cu as well as other metals that interact more strongly with graphene and thus direct the orientations of the graphene domains. But even growing graphene on these more promising metal substrates does not result in perfect crystals. Consequently, finding methods to heal defects in closed graphene layers will be pivotal for future efforts.

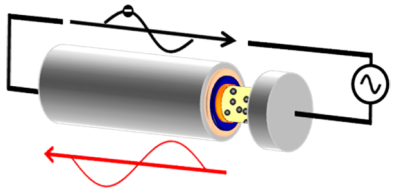
Toward this end, Günther *et al.* (DOI: 10.1021/nn303468j) used high-temperature scanning tunneling microscopy to investigate the ordering transition of amorphous carbon to graphene on Ru(001). The researchers first prepared a disordered carbon layer on the metal substrate by using chemical vapor deposition (CVD) of ethylene. Microscopy studies show that the carbon layer grows in dendritic islands of graphene-like density. Annealing leads to a coherent, but still disordered carbon layer. As the temperature rose to 920–950 K, the researchers found that small, round topographic holes appeared in the carbon layer, leaving behind ordered graphene in their wake as they moved around the field. Transport of carbon across or around the holes appears to be responsible for the ordering. The authors suggest that this mechanism could explain the difficulty in removing defects from chemically synthesized graphene, adding that researchers could improve graphene quality by introducing annealing periodically during CVD.



Nanocomposites Aim High for Sustained Capacitance and Frequency

Although metal particle dielectrics can have high permittivities, they generally require high-temperature sintering to process into multilayer thin films. On the other hand, polymer dielectrics are easier to process and have good dielectric strength, yet their low dielectric permittivities limit their applications. To get the best of both worlds, researchers have recently created inorganic-polymer nanocomposite materials, such as ceramic oxide particles in polymer matrices. Because these new materials have shown impressive permittivities and moderate stored energies, a next logical step is exploring analogous systems using metallic nanoparticles, which might be able to provide far higher capacitance than ceramic particles with easy processing. However, initial tests of materials, including gold- and silver-epoxy composites, have shown some drawbacks. While these composites have extremely high permittivities, their syntheses are limited to conventional mixing methods, and they have not been tested at high frequencies.

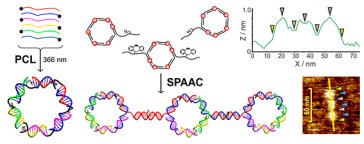
Trying a different tack, Fredin *et al.* (DOI: 10.1021/nn3044148) synthesized polypropylene nanocomposites by adsorbing an activated metallocene polymerization catalyst onto the native oxide surfaces present on metallic aluminum nanoparticles. These nanocomposites were randomly distributed at different concentrations into polyolefin matrices, creating films with no visible defects. As the volume fractions of Al nanoparticles increased, electrical measurements showed that the relative permittivity of the materials also increased, reaching about 10 at relatively low frequency. At the highest volume, measurements showed a high, sustained permittivity of greater than 6 for frequencies up to 7 GHz. The authors suggest that such materials could hold promise in a variety of next-generation electronic products.



Microfishing for Toxic Chemicals

Aquatic pollutants continue to be a pervasive environmental problem. One time-honored way to test water quality involves measuring changes in the swimming behavior and life expectancy of live fish when exposed to toxic substances. Although this method can provide qualitative and quantitative information on water contamination, it is associated with numerous drawbacks, including difficulty standardizing the organisms, problems with reproducibility, the requirement of skilled operators, and growing ethical qualms.

Seeking a new way to assess water quality that mimics live fish testing without using living organisms, Orozco *et al.* (DOI: 10.1021/nn305372n) developed artificial "microfish" whose motion is hindered by



a variety of major pollutants. These tiny cone-shaped swimmers rely on a catalase biocatalytic inner layer for forward propulsion. This enzyme must be active to access their hydrogen peroxide fuel. The researchers tested the performance of these microengines in solutions containing a variety of model pollutants representing heavy metals, pesticides, and herbicides, including Cu, Hg, NaN_3, and animotriazole. Visualizing the microfish under optical microscopy, they found that each of these pollutants hindered ejection of oxygen bubbles responsible for the swimmers' movements, attenuating their propulsion and significantly shortening the time they remained in motion. These results compared favorably to similar tests of swimming behavior and life expectancy in live fish. Also, like live-fish testing, movement and "life expectancy" of the microfish followed a dose–response relationship, with higher concentrations of pollutants leading to slower swimming and shorter times in motion. The authors suggest that these microfish could offer an alternative for water quality testing without the drawbacks of live fish.