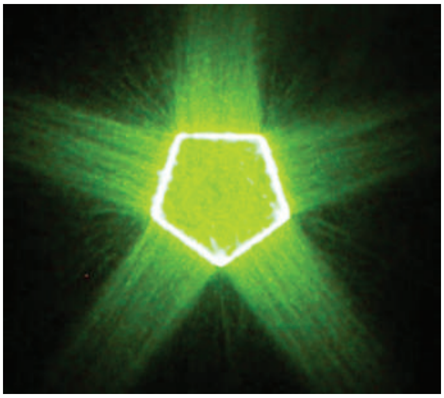
PLASMONS

Control on the edge

Nano Lett. **9,** 462–466 (2009)



© 2009 ACS / XIANG ZHANG

When electrons near the surface of a material oscillate in unison, they form electromagnetic waves called plasmons. Plasmons have potential for remote sensing, imaging, lithography and even cancer treatment, but they can be difficult to manipulate. Now, Xiang Zhang and co-workers at the University of California and Lawrence Berkeley National Laboratory have demonstrated a simple way of controlling plasmons using patterns cut into a thin metal film.

The researchers show that light from a mercury lamp can be converted into surface plasmons if it hits a sharp edge or slit in a material. This process diffracts the light into plasmons with a broad band of frequencies — plasmons generated in different places can interfere in any number of ways.

By cutting nanoscale slits in aluminium films — in patterns including triangles, squares and pentagons — the researchers demonstrated several different plasmon interference patterns. The plasmon patterns can be further tailored by adjusting the wavelength, polarization or incident angle of the light beam.

This accurate control of plasmons could lead to new methods of particle manipulation. It could also be used for 'sub-wavelength' imaging, because the plasmon interference patterns resolve features even smaller than the wavelength of the original light beam.

MAGNETIC RESONANCE IMAGING

Forcing the nanoscale

Proc. Natl. Acad. Sci. USA
doi:10.1073/pnas.0812068106 (2009)

Magnetic resonance imaging (MRI) can provide three-dimensional information on the structure and function of biological samples, but has so far been unable to resolve objects much smaller than a few micrometres in size. Now, Daniel Rugar and co-workers at IBM Research Division in San Jose, California have achieved MRI resolution as low as four nanometres, by improving the relatively new technique of magnetic resonance force microscopy (MRFM).

Their MRFM apparatus works by using a magnetic tip to excite nuclear magnetic resonance in samples deposited on a sensitive cantilever. The resonance generates tiny oscillations of the cantilever that can be detected using a laser interferometer.

To demonstrate, the researchers produced high-resolution images of tobacco mosaic viruses. The cantilever was oscillated by the continual flipping of proton spins in hydrogen atoms present in the virus proteins. The researchers then used sophisticated image-reconstruction software to convert the magnetic-force measurements into a three-dimensional map of proton density, which shows nanoscale details of the virus.

The images represent a 100-million-fold improvement in volume resolution over conventional MRI. The researchers suggest they could achieve better resolution, perhaps even lower than one nanometre, by applying more accurate force-detection techniques — to the point where MRI could probe the structure of individual molecules.

CASIMIR FORCES

Don't stick around

Nature **457,** 170–173 (2009)

The Casimir effect produces forces that are tiny, but this can be a nuisance in the design of nanoscale mechanical devices where it can make components stick together destructively. However, this can be turned around if the forces could be made repulsive instead of attractive — a theoretical possibility not shown until now. Federico Capasso at Harvard University and colleagues have measured the sought-after repulsive Casimir forces between a gold sphere and a silica plate immersed in fluid bromobenzene.

The group achieved this through their judicious selection of materials. In particular, bromobenzene was chosen for its dielectric permittivity, which is in between that of the other two materials — a necessary criterion to obtain repulsive Casimir forces. The measurements were carried out in an atomic force microscope fluid cell, where the gold sphere is attached to the cantilever. With a clever calibration technique that isolates hydrodynamic forces in the fluid, clean measurements of the repulsive Casimir forces between the gold sphere and the silica substrate are possible. These are turned into attractive forces when the substrate is replaced with gold.

This experiment is a long-awaited verification that repulsive Casimir forces exist and could point the way to practical design of ultra-low-friction devices and sensors.

NANOPARTICLES

Gold standard

Phys. Rev. Lett. **101,** 246103 (2008)

Nanoparticles can have strikingly different properties depending on their size, so it is important to have effective ways of measuring them. Ziyou Li and colleagues at the University of Birmingham have developed mass standards that could provide a quick and easy way of weighing nanoparticles and gaining insight into their fine structure.

The researchers previously developed a way of accurately estimating the mass of nanoparticles fired in a beam, by measuring their time-of-flight. They used this mass-selection technique to deposit several clusters of gold, with known numbers of atoms, onto graphite substrates.

The nanoclusters were observed using a scanning transmission electron microscope in high-angle annular dark field (HAADF) mode. The team found that the HAADF intensity of a cluster was monotonically dependent on the cluster size. This provided a calibration curve for 'weighing' other gold nanoparticles by measuring the HAADF intensity, and was tested on gold particles from both colloidal suspensions and thermal sublimation.

Once researchers know both the mass and size of a nanoparticle, they can get an idea of its shape and structure. This new technique could be especially important for industrial catalysts, whose performance is dependent on particles having complex shapes with a large surface area.

SELF-ASSEMBLY

Chain reaction

Science **322,** 1664–1667 (2008)

The self-assembly of molecular building blocks is frequently used to create new structures. When self-assembly is carried out on a solid surface, the structures formed can exhibit properties that are absent in the isolated constituent molecules. For example, the electronic states of connected species can delocalize, leading to increased electron mobility. Now, John Yates and colleagues at the University of Virginia, the

University of Pittsburgh, and the National Energy Technology Laboratory, Pittsburgh, have shown that self-assembly can also alter chemical reactivity.

The researchers examined dimethyldisulphide (CH_3SSCH_3) molecules, which can organize themselves into linear chains of up to 15 molecules on gold surfaces. Using the tip of a scanning tunnelling microscope (STM), electrons were injected into one end of a molecular chain, kick-starting a chemical reaction where successive sulphur–sulphur bonds dissociate and then reform to generate new dimethyldisulphide molecules.

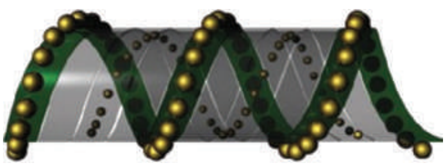
Through a combination of STM imaging and theoretical calculations, Yates and co-workers found that the activation energy required to break the sulphur–sulphur bond in dimethyldisulphide was reduced by at least a factor of five by self-assembly of the molecules. As a result, the chain reaction could propagate through as many as ten neighbouring molecules.

The team speculate that this discovery could lead to 'designer' assemblies, where chain reactions yield the required products through low-energy and stereospecific pathways.

DNA NANOTUBES

Gold control

Science **323,** 112–116 (2009)



Nanoparticles of a material can show optical, magnetic and electronic properties that are unattainable in their bulk form. By organizing such nanoparticles into precise and adjustable assemblies, the interactions between the nanoparticles, as well as with other molecular species, could be carefully controlled, potentially leading to new properties and applications. Now, Yan Liu, Hao Yan and colleagues at Arizona State University and the Scripps Research Institute have created complex three-dimensional architectures of gold nanoparticles using DNA-based self-assembly.

DNA has recently emerged as one of the most versatile molecular-scale building blocks, because it can be used to form tiles with 'sticky ends' capable of binding other tiles and directing the formation of a design. Through such means, two- and three-dimensional DNA nanostructures have been created, including nanotubes. Liu, Yan and co-workers have extended this work by attaching gold nanoparticles to single-stranded DNA to form tubules in a range of designs from stacked rings to spirals.

Using electron tomography, the researchers were able to identify the three-dimensional conformations of the nanotubes, showing, for example, a left-handed chirality in the spiral tubes. Furthermore, the nanoparticles were found to be active components in the assembly process, influencing the conformation of the nanotube through steric effects.

The researchers suggest that further developments in the design of DNA tiles may allow different sizes and types of nanoparticles to be accurately placed on the inside or outside of the tubes, leading to the development of advanced nanoscale devices.

LANTHANIDE NANOPARTICLES

Sensing danger

Angew. Chem. Int. Ed. **48,** 304–308 (2009)

Until now, terbium has been considered the best rare-earth metal for detecting anthrax spores because it is bright and has a long fluorescence lifetime. Lehui Le and co-workers from the Chinese Academy of Sciences in Changcun now show that europium-based nanoparticles are two orders of magnitude more sensitive and can discriminate anthrax from a host of interfering compounds more effectively than terbium.

The team modified the surface of fluorescein-doped silica nanoparticles with the ethylenediamine tetraacetic acid (EDTA) ligand and then converted the ligand into a europium complex. Europium served as the sensing molecule and fluorescein acted as a reference dye in the particle core; covalent binding of the dye and the europium minimized leaching and allowed efficient sensing with a low background signal. On addition of calcium dipicolinate — the unique biomarker of anthrax spores — the fluorescence of the nanoparticles increased in a concentration-dependent manner and changed from green to orange. The particles could detect the biomarker for anthrax spores down to 0.2 nM, which is much lower than the infectious dose of 60 μM. Moreover, the change in colour could be identified from as low as 1 μM, and time-dependent studies show the detection was complete in just 30 s.

This new study suggests europium-based nanoparticles compete well with terbium-based sensors and have the potential for rapid and ultrasensitive detection of anthrax spores in solution, with good selectivity over interfering compounds.

The definitive versions of these Research Highlights first appeared on the *Nature Nanotechnology* website, along with other articles that will not appear in print. If citing these articles, please refer to the web version.

Top down
Bottom up

Power from proteins

An interdisciplinary team has improved the performance of protein-based photovoltaic devices with a new kind of electrode.

Photosynthesis generates a remarkable 90 terawatts of power, with proteins such as photosystem I (PSI) having a central role in this process. The prospect that these proteins could be harnessed to generate electricity as a final product, rather than chemical energy, has motivated researchers to make them the active component of photovoltaic cells. Pursuing this goal, an interdisciplinary team at Vanderbilt University in Nashville, Tennessee has now attached PSI to nanoporous gold-leaf electrodes as part of an electrochemical photovoltaic cell (*ACS Nano* doi: 10.1021/nn800389k; 2009). The high surface-area of the modified electrodes allows for a greater density of proteins, which increases the photocurrent by a factor of three, compared with the same cell using planar electrodes.

The collaboration began through the Vanderbilt Institute for Nanoscale Science and Engineering (VINSE), which was set up to bring together faculty and students across the university. It was through VINSE that Kane Jennings, a professor in the department of chemical and biomolecular engineering, met David Cliffel, a chemistry professor and an expert on electrochemistry and electron transfer. Peter Ciesielski, the first author on the paper, is a graduate student in Vanderbilt's Interdisciplinary Materials Science Program.

Neither Jennings nor Cliffel had much of a biology background: "We both had to learn the biology, and we are still learning the biology." admits Jennings. Nor was the development straightforward: "The error bars in biology are typically quite a bit larger than those in chemical engineering and chemistry. Approximately two years of work was required to obtain consistent properties from [the photosynthetic proteins]". But it was worth it. "The accompanying infusion of new ideas is an exciting reprieve," says Jennings, "because staying within one's comfort zone can become boring after a few years."