photocurrent spectra. The efficiency of this system was then improved through the introduction of metallic nanoparticles to alleviate poor charge transport and concentrate incident sunlight close to the semiconductor–liquid interface (see figure).

First, 50-nm Au nanoparticles with a thin, nonreactive silica shell were either covered with a 100-nm thick iron-oxide film or deposited on top of a 90-nm thick iron-oxide film. When nanoparticles were located on the bottom and on the top of the film, strong photo enhancements were observed for wavelengths longer than 550 nm. The strongest resonance peak enhancement was obtained at 610 nm and 590 nm, with enhancements of 11 and 20 times, respectively, over the photocurrents observed for films without nanoparticles.

In order to investigate a more nearly ideal optical system, the researchers repeated the experiments and simulations with uncoated Au nanoparticles. While a symmetrical photo enhancement as a function of wavelength was observed when the nanoparticles were located at the bottom of the iron-oxide film, an asymmetric photo enhancement was found when the nanoparticles were on top of the film. This difference was attributed to interference between the incident light wave and the scattered fields from the nanoparticles.

The researchers said, "We anticipate that the concepts described here will also be highly relevant to the development of future, more effcient, multi-junction photoelectrochemical cells, where sunlight is split into multiple spectral components, each of which requires its own optical tailoring and enhancement strategies."

Steven Trohalaki

Bio Focus

Three-dimensional plasmon ruler enables measurement of macromolecules

Three-dimensional (3D) plasmon rulers, capable of measuring nanometer-scale spatial changes in macromolecular systems, have been developed by researchers at Lawrence Berkeley National Laboratory (Berkeley Lab) in collaboration with researchers at the University of Stuttgart, Germany. These 3D plasmon rulers could provide scientists with the opportunity to obtain unprecedented information on critical dynamic events in biology such as the interaction of DNA with enzymes, the folding of proteins, the motion of peptides, or the vibrations of cell membranes.

"We've demonstrated a 3D plasmon ruler, based on coupled plasmonic oligomers in combination with high-resolution plasmon spectroscopy, that enables us to retrieve the complete spatial configuration of complex macromolecular and biological processes, and to track the dynamic evolution of these processes," said Paul Alivisatos, director of Berkeley Lab and leader of this research.

Alivisatos, Laura Na Liu now at Rice University, and Mario Hentschel, Thomas Weiss, and Harald Giessen of the University of Stuttgart reported their findings in the June 17 issue of *Science* (DOI: 0.1126/science.1199958; p. 1407).

The nanometer scale is where the biological and materials sciences converge. As human machines and devices shrink to the size of biomolecules, scientists need tools by which to precisely measure minute structural changes and distances. To this end, researchers have been developing linear rulers based on the electronic surface waves known as "plasmons," which are generated when light travels through the confined dimensions of noble metal nanoparticles or structures, such as gold or silver.

"Two noble metallic nanoparticles in close proximity will couple with each other through their plasmon resonances to generate a light-scattering spectrum that depends strongly on the distance between the two nanoparticles," Alivisatos said. "This light-scattering effect has been used to create linear plasmon rulers that have been used to measure nanoscale distances in biological cells."

Compared to other types of molecular rulers, which are based on chemical dyes and fluorescence resonance energy transfer (FRET), plasmon rulers neither blink nor photobleach, and also offer exceptional photostability and brightness. However, until now, plasmon rulers could only be used to measure distances along one dimension, which is a limitation that hampers the development of any comprehensive understanding of biological or general soft-matter processes that take place in three dimensions.

"Plasmonic coupling in multiple nanoparticles placed in proximity to each other leads to light scattering spectra that are sensitive to a complete set of 3D motions," said Liu. "The key to our success is that we were able to create sharp spectral features in the otherwise broad resonance profile of plasmon-coupled nanostructures by using interactions between quadrupolar and dipolar modes."

Liu said that typical dipolar plasmon resonances are broad because of radiative damping. As a result, the simple coupling between multiple particles produces indistinct spectra that are not readily converted into distances. The research team overcame this problem with a 3D ruler constructed from five gold nanorods of individually controlled length and orientation, where one nanorod is placed perpendicular between two pairs of parallel nanorods to form a structure that resembles the letter H.

"The strong coupling between the single nanorod and the two parallel nanorod pairs suppresses radiative damping and allows for the excitation of two sharp quadrupolar resonances that enable high-resolution plasmon spectroscopy," Liu said. "Any conformational change in this 3D plasmonic structure will produce readily observable changes in the optical spectra."

Not only did conformational changes in the 3D plasmon rulers alter light-scattering wavelengths, but the degrees of spatial freedom afforded by its five-nano-

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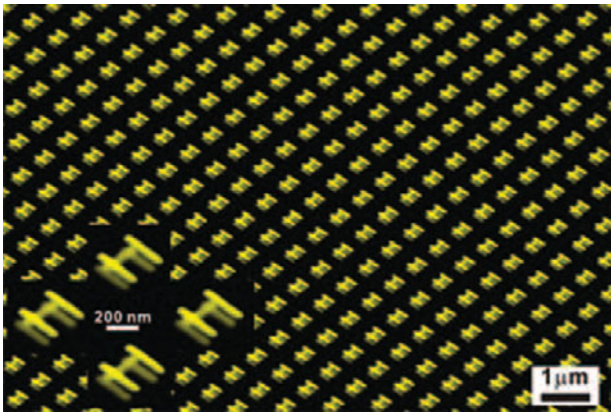


Scanning electron micrograph of a three-dimensional plasmon ruler fabricated from gold nanorods by electron beam lithography.

rod structure also enabled the research team to distinguish the direction as well as the magnitude of structural changes.

"As a proof of concept, we fabricated a series of samples using high-precision electron-beam lithography and layer-by-layer stacking nanotechniques, then embedded them with our 3D plasmon rulers in a dielectric medium on a glass substrate," Liu said. "Experimental results were in excellent agreement with the calculated spectra."

The researchers envision a future in which 3D plasmon rulers would, through biochemical linkers, be attached at different positions to a sample macromolecule, such as a strand of DNA or RNA, or a protein or peptide. The sample macromolecule would then be exposed to light and the optical responses of the 3D plasmon rulers would be measured through dark-field microspectroscopy.

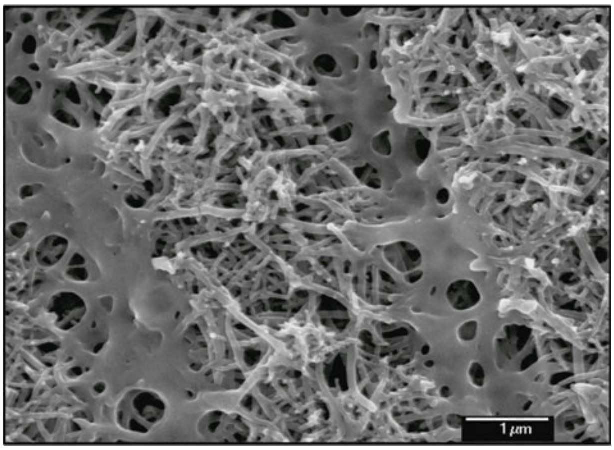
"The realization of 3D plasmon rulers using nanoparticles and biochemical linkers is challenging, but 3D nanoparticle assemblies with the requisite symmetries and configurations have already been demonstrated," Liu said. "We believe that these exciting experimental achievements and the introduction of our new concept will pave the road toward the realization of 3D plasmon rulers in biological and other soft-matter systems."

Nano Focus

IR lasers enable direct patterning on conjugated polymers

A versatile and simple new technique for patterning submicrometer features in a conjugated polymer using an infrared laser is described in the August 10 issue of *Nano Letters* (DOI: 10.1021/nl2011593; p. 3128). While the potential for low-cost processing is a key advantage of using organic semiconductor materials in the place of conventional silicon electronics, many patterning techniques used at present such as contact printing and dip-pen lithography are either time-consuming or expensive. In their recent article, R. Kaner from the University of California–Los Angeles, G. Wallace of the University of Wollongong, Australia, and co-workers demonstrate how a laser in a commercial disk drive can be used to write features with tunable conductivity onto polyaniline-coated discs.

The team made use of a commercially available program normally used to create images on a compact disc, by activating a dye coating with a 788 nm laser. By replacing this coating with the well-known conductive polymer polyaniline, features could instead be written into the polymer by thermally inducing cross-linking at the irradiated regions. The high photothermal conversion efficiency and poor thermal conductivity of polyaniline allows the laser to induce highly localized melting of the polymer fibers into visibly welded regions as thin as 1 μm. Chemical cross-linking between neighboring fibers is proposed to occur through the formation of heterocycles containing two nitrogen atoms from adjacent chains, and the accompanying rearrangement of carbon double bonds can be clearly observed by the change in infrared spectra.



A scanning electron micrograph of a polyaniline film with lines of cross-linked polymer formed by an infrared laser. Reproduced with permission from *Nano Lett.* (DOI: 10.1021/nl2011593; p. 3128). © 2011 American Chemical Society.

The program's facility for creating grayscale images by varying the intensity of the laser could also be neatly translated into controlling the conductivity of the polyaniline features. At maximum laser intensity, the irradiated regions were rendered electrically insulating by the cross-linking, but as the intensity was lowered, a range of intermediate resistances from insulating to metallic could be achieved. Corresponding changes in the emission spectrum and reflectivity of the polymer film also allowed the team to create high-resolution color images, which could be varied in a myriad of ways by altering the polymer's oxidation state or through the addition of chemical substituents.

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