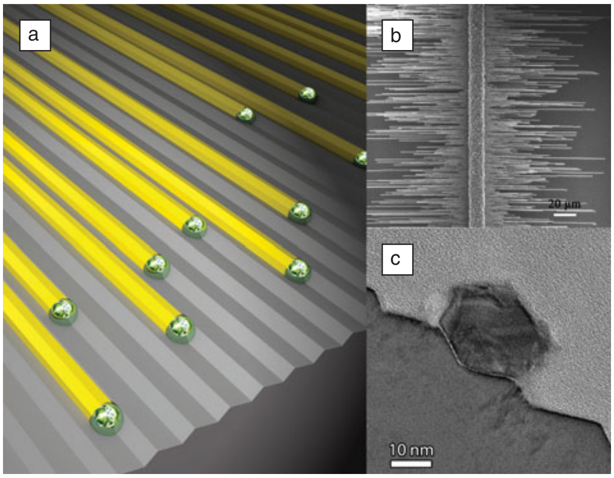
nanowires grew in random triangular patterns following six isomorphic directions. However, on a 2° miscut *c*-plane, the nanowires grew along only two directions, forming parallel arrays.

"We found that when the substrate is cut in a slightly tilted or unstable plane," Joselevich said, "the surface wrinkled up upon heating, and the tiny steps and grooves that formed on it made the alignment of the nanowires much better than on a smooth surface." Or, as the researchers reported in their article, "graphoepitaxy overrules epitaxy."

The researchers report that their GaN nanowires have few defects and that they exhibit excellent optical and electronic properties, which makes them potential candidates for nanoscale high-power circuits, light-emitting diodes, lasers, photovoltaic cells, photodetectors, and radio-frequency, photonic, and nonlinear optical devices. The relative absence of defects is atypical for semiconductors grown on a substrate, because stresses usually develop that produce defects.

"We think this is because, unlike a two-dimensional film, which usually gets stressed, a nanowire can relax by shrinking or swelling sidewise, making the system much more tolerant to mismatch than one is used to seeing in continuous two-dimensional films," Joselevich said. "This is a new one-dimensional nanoscale effect, which, together with the effect of graphoepitaxy, somehow changes the paradigm not only in the new field of nanowires, but also in the well-established fields of epitaxy and thin films."



(a) Illustration of nanowires growing along nanogrooves; (b) top view of the nanowires by scanning electron microscopy; and (c) cross-section view of a nanowire along a V-shaped nanogroove by transmission electron microscopy. *Image credit*: Ernesto Joselevich.

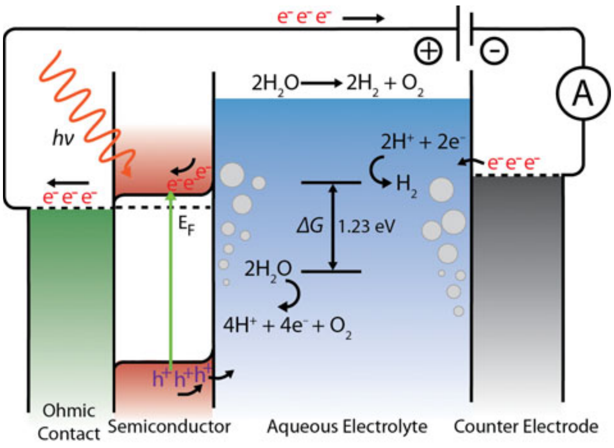
Tim Palucka

Energy Focus

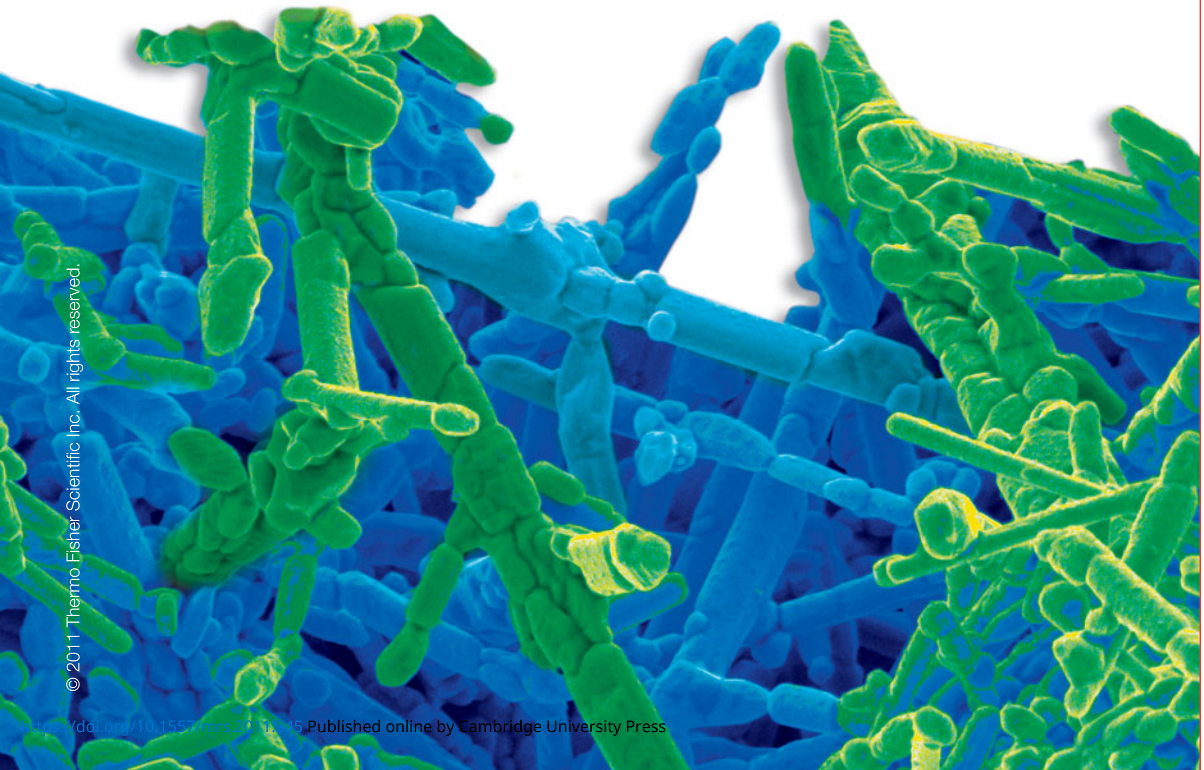
Surface plasmons used to enhance solar-to-fuel energy conversion

Efforts to develop technologies for solar water splitting based on inexpensive, earth-abundant materials date back to the 1970s. Efficiencies of developed systems, however, remain low. One source of this inefficiency is the mismatch between the length scales of the key events; photon absorption occurs up to a few microns, while electron-carrier extraction is limited to several tens of nanometers. Photoexcited carriers are therefore generated too far from a reactive surface, and recombine before they can be converted to fuel. One general approach used to overcome this problem is the design of structured materials where the photon propagation and charge-transport directions are orthogonal to each other. Recently, I. Thomann and B.A. Pinaud from Stanford University and their colleagues showed that plasmonic resonances from metallic nanospheres can be combined with multilayer interference effects to better manage photons for more efficient solar conversion.

Collective electron oscillations in metallic nanoparticles are termed surface plasmons, and their resonance frequencies can be tuned from UV to near IR by changing the nanoparticle size, shape, and dielectric environment. As reported in the August 10 issue of *Nano Letters* (DOI: 10.1021/nl201908s; p. 3440), the research team employed the existing knowledge-base of plasmon-enhanced photovoltaics to demonstrate that plasmonics can enhance solar energy conversion to fuels. The researchers used a typical solar cell comprising an iron-oxide (α-Fe_2O_3) photoelectrode to measure wavelength-dependent photocurrents and therefore to determine the



This schematic of the band diagram shows the semiconducting electrode absorbing sunlight while in contact with an aqueous electrolyte solution in which photogenerated holes cause O_2 and electrons to be generated. The electrons are transported to a counter electrode where they react to produce H_2 and close the circuit. The researchers used α-Fe_2O_3 together with metallic nanoparticles as the semiconducting electrode, and measured the photogenerated current as a function of illumination wavelength. Reproduced with permission from *Nano Lett.* (DOI: 10.1021/nl201908s; p. 3440). © 2011 American Chemical Society.



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-