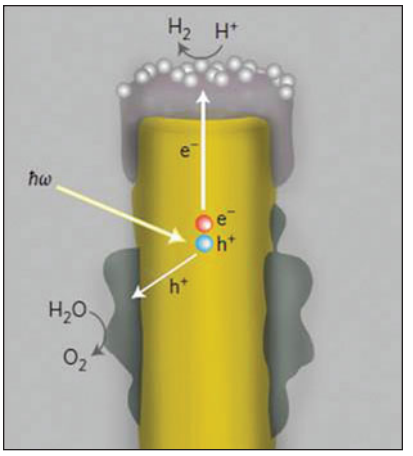
Energy Focus

Autonomous plasmonic solar water splitter displays long-term stability

Fuels, and in particular hydrogen, generated through the conversion of solar energy, may eventually provide a replacement for fossil fuels. Solar conversion based on electron–hole pair production in semiconductors is currently the focus of substantial scientific and commercial interest. It has recently been suggested that charge carriers transferred from a plasmonic structure to an adjacent semiconductor or photocatalyst can result in enhanced photoconversion, providing a new paradigm for harvesting photons. Although the strong wavelength dependence of the surface plasmon excitation makes it possible to design plasmonic devices capable of harvesting photons over the entire solar spectrum, most current systems show small photocatalytic activity in the visible range as compared to the ultraviolet. Recently, however, M. Moskovits and a team of researchers from the University of California–Santa Barbara, fabricated an autonomous solar water-splitting device in which all charge carriers derive from surface plasmons.

In a letter to *Nature Nanotechnology* published online February 24, 2013 (DOI: 10.1038/NNANO.2013.18), Moskovits and co-researchers described their device, which was comprised of a uniform array of aligned Au nanorods that serve as light-harvesting antennae, capped with crystalline TiO_2. A metal-semiconducting Schottky junction is therefore formed that has a much lower junction voltage than a *p–n* junction, and an almost nonexistent depletion width in the metal. The exposed portions of the nanorods are decorated with a Co-based O_2-evolution catalyst, which enhances O_2 evolution (see Figure). Functioning without external wiring, each nanorod produces 5×10^{13} H_2 molecules/cm^2-s under 1 sun illumination with the photocathode immersed in 1 M KBO_3 electrolyte (pH 9.6). The device displayed remarkable stability—no significant decrease in activity was observed after 11 6-h cycles.



This cross-sectional schematic of an individual plasmonic solar water splitter unit consists of a gold nanorod, the TiO_2 cap (decorated with platinum nanoparticles)—which functions as the H_2 evolution catalyst—and the Co-based O_2 evolution catalyst deposited on the lower portion of the gold nanorod. Reproduced with permission from *Nature Nanotech.* **8** (2013), DOI: 10.1038/NNANO.2013.18; p. 247. © 2013 Macmillan Publishers Ltd.

The researchers said that the plasmons excited on the Au surface decay on a femtosecond time scale and produce electron–hole pairs. A significant fraction of the hot electrons, that is, those with sufficient kinetic energy, transiently occupy states in the Au's conduction band, which are normally vacant. Reaching the nanorod surface, they enter the conduction band of the TiO_2, which acts as an electron filter and not as a participant in the light conversion process. The external quantum efficiency is ~0.1% for the visible spectrum but rose to ~0.25% when the device was exposed to the full solar spectrum. Although high compared to other plasmonic devices, these efficiencies are too low for practical devices. However, the researchers said, "Straightforward structural improvements to the device we describe can lead to significant efficiency improvements. For example, the coverage of the Pt hydrogen evolution catalyst can be improved by increasing the spacing between the nanorods to allow a larger fraction of the nanorods' surface to be processed, with a simultaneous increase in the nanorods' length to ensure that the array's plasmonic absorption remains high."

Steven Trohalaki