Using plasmons to harness the sun’s energy for fuel

Martin Moskovits

Photoexciting nanostructured metals and building a device that splits water into hydrogen and oxygen is a radically new way to convert sunlight directly into fuel.

Converting sunlight into electricity is a mature science and a lucrative business, normally carried out in photodiodes based on semiconductor materials. Artificial photosynthesis—using sunlight to power the autonomous conversion of reactants to higher free-energy products, mimicking the way plants and phytoplankton convert carbon dioxide (CO$_2$) and water to sugars—has not yet evolved sufficiently to be commercialized. This is because an autonomous, light-driven device that splits water into dihydrogen (H$_2$) and dioxygen (O$_2$), as first reported by Fujishima and Honda,$^1$ that is robust enough to function unattended for many months is normally based on a wide-bandgap semiconductor. Such a device makes use only of the UV part of the sun’s spectrum and is consequently very inefficient. Devices based on narrow-bandgap semiconductors or on organic dye-sensitized titanium oxide (TiO$_2$) are unsuitable because they either photocorrode or photobleach, which often reduces their working lifetimes to mere minutes.

Recently Mubeen et al.$^2$ reported an autonomous water splitter based largely on metal rather than on semiconductors. Photosynthesis, an example of redox photochemistry, involves reduction and oxidation acting together. In water splitting, the conversion of hydrogen ions to hydrogen molecules is the reduction. The lost electron is then returned in an oxidation reaction such as the formation of neutral oxygen from negatively charged hydroxyl ions. In semiconductors, electrons and holes (the pseudo-positive absence of an electron) arise from a quantum transition promoting an electron from a populated energy band across the bandgap to an empty, higher-energy band, forming a so-called exciton, an electron-hole pair. An internal voltage difference thereby created encourages the electrons and holes to migrate in opposite directions and, it is hoped, reach different interfaces where they can carry out their respective chemistries before they recombine and lose that ability.

Figure 1. Schematic of a plasmonic water splitter built around an array of aligned gold nanorods, each furnished (as illustrated by one of the nanorods in the foreground) with appropriate catalyst materials to carry out the reduction of water to hydrogen gas (near its tip) and the oxidation of water to oxygen gas (near its base).$^2$ A photon of visible light, $\hbar\nu$, excites a surface plasmon, which decays into an electron (e$^-$) and a hole (h$^+$). The former migrates to the platinum nanoparticles near the top of the nanorod where it converts H$^+$ to dihydrogen. The latter makes use of the cobalt borate catalyst near the base of the nanorod to produce dioxygen. Artwork by Sylvia (Joun) Lee.

In our all-metal system$^2$ (see Figure 1) fashioned around a dense array of aligned gold nanorods, the electrons do not result from the creation of excitons in a semiconductor. Instead, the light drives collective excitations of the entire ensemble of the conduction electrons, called surface plasmons (SPs), that rattle back and forth for a few femtoseconds before dephasing, at which point one or more very energetic electrons—hot electrons—carry away most of the plasmon’s energy. Unless one can put the hot electrons to work first, the plasmon’s energy will ultimately be converted to heat.

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In principle, an enormous number of hot electrons can be produced in this manner. With an $\sim 10^6$ fs SP lifetime, $\sim 10^{14}$ hot electrons can be created per second in each of our gold nanorods. With a nanorod density $\sim 10^{10}$ aligned gold nanorods per cm$^2$ of surface, one can produce as many as $1 \times 10^{24}$ hot electrons per second per cm$^2$. The trick, however, is to extract a significant fraction of these electrons and put them to work toward some useful purpose—for example, by terminating one end of the nanorods with a platinum catalyst that helps the electrons react with hydrogen ions in water to evolve hydrogen gas, while covering the other end of each nanorod with a cobalt borate catalyst that uses the positive charges left behind in the gold to convert hydroxyl ions into oxygen. The device produces hydrogen almost entirely on account of light absorbed by the SP resonances of the gold nanorods, as shown by the fact that its photoelectrochemical activity tracks the extinction spectrum of the gold nanorods faithfully. It produces approximately 63 standard temperature and pressure milliliters of H$_2$ per hour per gram of catalyst and has been operated without failure over many weeks of observation. This corresponds to a power conversion efficiency $\sim 0.25\%$, a good start that we think can be improved upon in multiple ways—for example, by increasing the fraction of the surface of the nanorod that is covered by catalyst and by improving the nanorod spacing so as to prevent the evolved gas from blocking water access to the nanorods.

For most metals, the SP resonance lies in the UV spectrum. For gold, silver, and copper, the SP is particularly intense and occurs in or near the visible region of the spectrum, and its precise frequency can be tuned by changing the nanostructure’s geometry, by embedding it in a dielectric material, or both. The greater the material’s dielectric constant, the larger the SP’s wavelength shift. For gold nanorods, the longitudinal SP resonance can be tuned from $\sim 500$ nm well into the IR by increasing the nanorod’s length. A judiciously fabricated assembly of gold nanowires could cover the entire visible and IR portions of the sun’s spectrum, taking full advantage of the sunlight’s energy.

In addition to our group, there are many others worldwide currently exploiting the promise of surface plasmons in solar energy applications.

Author Information

Martin Moskovits
University of California-Santa Barbara
Santa Barbara, CA

Martin Moskovits is professor of chemistry at UC-Santa Barbara where he served as dean of science from 2000 to 2007. From 2007 to 2010, he was chief technology officer of API Technologies Corp. and co-founded Spectra Fluidics, an organization that fabricates surface-enhanced Raman spectroscopy-based microfluidic sensors. His research focuses on plasmonics and energy.

References