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Hot Electrons Cross Boundaries

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put, including high pore density, pore continuity, and the ability to form defect-free thin films. Several of the approaches listed above form 1D columnar pores (*6*, *9*–*12*) that need to be aligned in the flow direction and packed closely together for high membrane flux. Materials with 3D-interconnected pores (*7*, *8*, *13*–*15*) have the advantage that the pores need not be aligned to be continuous across the membrane, and are not easily blocked. These materials also often have better overall pore densities. Although many of the above materials can be processed into films, only a handful have been formed into films thin enough (*6*, *8*, *11*, *12*, *14*) to achieve high fluxes (i.e., thinner membranes have less flow resistance). For researchers working on new dense or porous materials for membrane applications, it is important to consider not only the design factors that afford better separation selectivity but also the factors that afford good productivity.

The future directions for these new membrane materials are very promising, primarily because of the enormous chemical flexibility of their base structures. The separation properties for the application of interest can be tuned, as can operational parameters such as stability and longevity. In addition, functional additives such as selective complexing agents can be incorporated into these new classes of membrane materials, providing exciting new opportunities for enhancing separation performance.

References

1. W. J. Koros, *Chem. Eng. Prog.* **91**, 10 (1995).
2. L. M. Robeson, *J. Membr. Sci.* **320**, 390 (2008).
3. J. E. Bara, D. E. Camper, D. L. Gin, R. D. Noble, *Acc. Chem. Res.* **43**, 152 (2010).
4. B. A. Voss, J. E. Bara, D. L. Gin, R. D. Noble, *Chem. Mater.* **21**, 3027 (2009).
5. K. Simons, K. Nijmeijer, J. E. Bara, R. D. Noble, M. Wessling, *J. Membr. Sci.* **360**, 202 (2010).
6. M. Wirtz *et al.*, *Int. J. Nanosci.* **1**, 255 (2002).
7. Y. C. Hudiono, T. K. Carlisle, A. L. LaFrate, D. L. Gin, R. D. Noble, *J. Membr. Sci.* **370**, 141 (2011).
8. T.-H. Bae *et al.*, *Angew. Chem. Int. Ed.* **49**, 9863 (2010).
9. B. J. Hinds *et al.*, *Science* **303**, 62 (2004).
10. T. Xu *et al.*, *ACS Nano* **5**, 1376 (2011).
11. K. F. Czaplewski, J. T. Hupp, R. Q. Snurr, *Adv. Mater.* **13**, 1895 (2001).
12. X. Yan, V. Janout, J. T. Hsu, S. L. Regen, *J. Am. Chem. Soc.* **124**, 10962 (2002).
13. M. Zhou *et al.*, *J. Am. Chem. Soc.* **129**, 9574 (2007).
14. D. A. Olson, L. Chen, M. A. Hillmyer, *Chem. Mater.* **20**, 869 (2008).
15. M. R. Newton, A. K. Bohaty, H. S. White, I. Zharov, *J. Am. Chem. Soc.* **127**, 7268 (2005).

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APPLIED PHYSICS

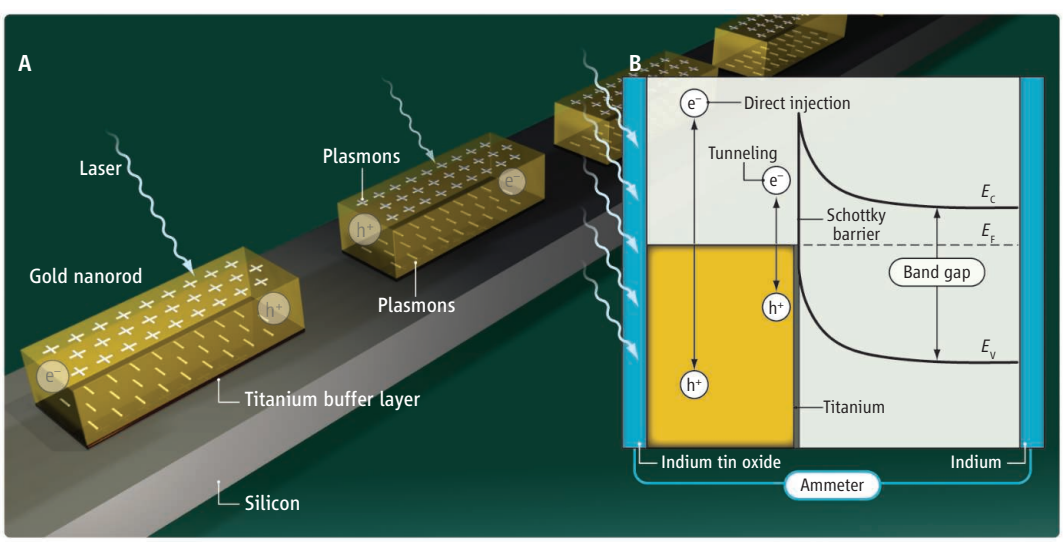
Hot Electrons Cross Boundaries

Devices based on gold nanostructures that convert absorbed light into electrical current can be used to detect near-infrared light.

Martin Moskovits

When light hits the surface of gold or silver, it can excite collective oscillations of the conduction electrons called surface plasmons. The sensitivity of surface plasmons to changes in the surface region forms the basis of analytical tools such as surface plasmon resonance detection, which can be used in lab-on-a-chip applications to detect biomolecules. The excitation of surface plasmons also underlies surface-enhanced Raman spectroscopy. The surface plasmon of silver and gold surfaces that are rough at a nanoscale greatly increases local electric fields and boosts the signal from adsorbed molecules. The wavelength that excites surface plasmons can also be tuned by creating nanoparticles of different sizes, and on page 702 of this issue, Knight *et al*. (*1*) exploit this effect to create a detector for near-infrared light. They fabricated a device consisting of rod-like nanoantennas that harvest light and convert a portion of the resulting plasmonic energy into an electric current without the need for an applied bias voltage.

The fundamental mode of the surface plasmons is similar to that of a quantum harmonic oscillator—a sea of electrons oscillates and creates alternating regions of higher electron density (that is relatively negatively charged) and lower electron density (that is relatively positively charged; see the figure, panel A). Many quanta of



Plasmons to electricity. (**A**) Light excites surface plasmons (depicted as regions of positive and negative charge, top and bottom) that can decay into charge carriers, electrons e^- and holes h^+. Plasmons in shorter nanorods are excited at shorter wavelengths. The nanorods were grown on a titanium (Ti) buffer layer, 1 nanometer thick, on n-type silicon. (**B**) An energy diagram showing how excited electrons created by plasmon decay encounter a Schottky barrier at the metal-silicon interface, which share a common Fermi energy E_F. Highly energetic electrons are either directly injected into the conduction band of silicon above its band edge, E_c, or tunnel through the barrier. The barrier is less than the band gap energy (the difference between E_c and valence band edge, E_v). Holes and electrons produce a measurable photocurrent collected at the indium tin oxide and indium electrodes.

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the incoming light can be stored in the plasmonic oscillator, even when it is illuminated with dim light. In the tetragonal gold nanorods used by Knight *et al*., the plasmon resonance wavelengths are in the near-infrared, and shorter nanorods will have a shorter peak wavelength.

The light quanta stored in the plasmons can be re-emitted as light, but some of the plasmons can also decay into two charge carriers, an electron and a "hole." It has been known for some time that plasmon decay can create "hot" electrons that have high kinetic energy (*2*). However, to create a photocurrent, the electron and hole must be separated. Knight *et al*. extracted the electron into n-type silicon, which has high conductivity for electrons (see the figure, panel B). Normally, these hot electrons would still not have enough energy to enter the conduction band of silicon if they were starting their journey in the occupied molecular orbitals (valence band) of silicon—the energy gap is 1.1 electron volts. The electrons only need to clear a barrier set up at the metal-silicon interface (known as a Schottky barrier; in this case, a barrier of 0.5 electron volt is created by a thin layer of titanium metal used to adhere the gold nanorods). The most energetic fraction of the hot electrons either clear the Schottky barrier, or quantum-mechanically tunnel through it into the conduction band of silicon.

Quantum-mechanical tunneling depends not only on barrier height but also on its breadth. Tunneling is enhanced in this device because the barrier decreases as the electron moves into the silicon, an effect called conduction-band bending. Because the electrons have high kinetic energy, they need travel only a short distance beyond their point of generation before they become conduction electrons in silicon—too short a distance for them to lose energy through other relaxation processes. They then become trapped in the semiconductor by the barrier.

Plasmonic systems can be designed to cover much of the solar spectrum, so this approach suggests a photosensitization strategy, much like the one exploited by Grätzel in dye-sensitized photovoltaics (*3*), but avoiding the problem of easily photodegradable organics. Although Knight *et al*. report very low quantum efficiencies, there is no physical reason why efficiencies cannot be much larger and lead to applications in energy conversion and photodetection.

References

1. M. W. Knight, H. Sobhani, P. Nordlander, N. J. Halas, *Science* **332**, 702 (2011).
2. V. M. Shalaev, C. Douketis, J. T. Stuckless, M. Moskovits, *Phys. Rev. B* **53**, 11388 (1996).
3. M. Grätzel, B. O'Regan, *Nature* **353**, 737 (1991).

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IMMUNOLOGY

Flow Cytometry, Amped Up

The novel technique of mass cytometry opens a new chapter in single-cell biology.

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In multicellular organisms, cells carry out a diverse array of complex, specialized functions. This specialization occurs mostly through the expression of cell type–specific genes and proteins that generate the appropriate structures and molecular networks. A central challenge in the biomedical sciences, however, has been to identify the distinct lineages and phenotypes of the specialized cells in organ systems, and track their molecular evolution during differentiation. On page 687 of this issue, Bendall *et al*. (*1*) offer a brilliant proof of principle for a novel technology—mass cytometry—and provide a uniquely detailed view of cell differentiation in the human hematopoietic system. They used this technology to simultaneously examine 34 attributes of human bone marrow cells and then create a superimposed map showing the complex interactions of cell signaling molecules, all at an unprecedented level of resolution. This opens a new chapter in single-cell biology.

Since the 1970s, fluorescence-based flow cytometry has been the leading technique for studying and sorting cell populations (*2*). It involves passing cells through flow chambers at high rates (>20,000 cells/s) and using lasers to excite fluorescent tags ("fluorochromes") that are usually attached to antibodies; different antibodies are tagged with different colors, enabling researchers to quantify molecules that define cell subtypes or reflect activation of specific pathways. Progress in instrument design, multilaser combinations, and novel fluorochromes has led to experimental configurations that simultaneously measure up to 15 markers. This has enabled very detailed description of cell subtypes, perhaps most extensively in the immune system, where the Immunological Genome Project is profiling >200 distinct cell types. Fluorescence cytometry seems to have reached a technical plateau, however: In practice, researchers typically measure only 6 to 10 cell markers because they are limited by the spectral overlap between fluorochromes (see the figure).

To escape this plateau, a group led by Scott Tanner of the University of Toronto in Canada devised the radically new approach of mass cytometry (CyTOF) (*3*), and teamed with a group led by Garry Nolan of Stanford University in California, who has long been a leader in developing higher-dimensional multicolor flow cytometry, especially for studying intracellular signaling components (*4*). In mass cytometry, fluorochrome tags are replaced by a series of rare earth elements (e.g., lanthanides), which are attached to antibodies through metal-chelator coupling reagents. Cells are labeled by incubation in a cocktail of tagged antibodies; as the cells flow through the instrument, they are vaporized at 5500 K, and the released tags are identified and quantified by time-of-flight mass spectrometry (MS). Rates are reasonable, at 1000 cells/s. The beauty of the approach stems from three factors: the precision of MS detection, which eliminates overlap between tags (a dream for any investigator who has battled this problem, known as fluorescence compensation); the number of detectable markers (34 here, but easily more); and the absence of background noise (because rare earth elements are essentially absent from biological materials, there is no equivalent of "autofluorescence"). Because the software tools commonly used for flow cytometry data would be woefully inadequate for analyzing dozens of dimensions, Bendall *et al*. used software that clusters cell populations into "minimum-spanning trees" that reproduce known hematopoietic differentiation, but with much finer granularity. As a result, cells that once would

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