Designing the Next Generation of Chemical Separation Membranes

Douglas L. Gin, *et al.*

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(*5*). It may be possible to use this inhibitory pathway to therapeutic advantage, because selective electrical stimulation of the vagus nerve inhibits the production of tumor necrosis factor, interleukin-1 and other cytokines, and prevents the pathology associated with arthritis, colitis, ischemic tissue injury, and other syndromes in experimental models.

Sun *et al*. reveal that neural control of innate immunity in mammals is present in *Caenorhabditis elegans*, one of the simplest organisms with a nervous system. This indicates that the regulatory mechanism dates back to the origins of the nervous system. *C. elegans* is a soil nematode, ~1 mm in length, that feeds on bacteria in decaying vegetable matter. Its nervous system consists of only 302 sensory neurons, motor neurons, and interneurons. The neurotransmitters include acetylcholine and γ-aminobutyric acid, which facilitate locomotion and pathogen avoidance. The authors found that worms lacking a cell surface receptor called OCTR-1 in two types of neurons exhibit substantially improved survival against the bacterial pathogen *Pseudomonas aeruginosa*. These neurons—the "ASH" and "ASI" sensory neurons—extend processes into an opening at the anterior end of the worm, where they are exposed to the environment. The protection was observed in the presence of living, but not dead bacteria, indicating that these neurons inhibit the innate immune response to bacterial pathogens. The protection was not attributed to enhanced pathogen avoidance, or pathogen accumulation. Rather, the neurons targeted, in nonneuronal cells, the molecular basis of the unfolded protein response, a mechanism that regulates organellar (endoplasmic reticulum) accumulation of unfolded proteins during periods of heightened protein synthesis, as in infection. Together, these results show that the tonic output of innate immunity is negatively regulated by signals originating in ASH and ASI sensory neurons in the worm (see the figure). Hence, in worms, as in mammals, the innate immune system is not autonomous; it is innervated. Additional work is needed in the worm model of Sun *et al*. to determine the nature of the signals that activate OCTR-1, a putative catecholamine receptor, in sensory neurons. Further work should also reveal how the sensory neurons regulate the unfolded protein response pathway in nonneuronal cells.

How might such a neural controlling system operate, and what are the possible therapeutic implications? A general principle in physiology is that innervation of a system enables reflex control mechanisms to provide a regulatory framework that can fine tune responses over time and space. The inflammatory reflex, a prototypical circuit in mammals, is activated by exposure to pathogens or injury and modulates the innate immune response (*5*). Neurons express Toll-like receptors and cytokine receptors, which detect the presence of pathogens (and perhaps damaged tissue as well) and cytokines, respectively (*6*, *7*). This activates action potentials that ascend to the central nervous system, which in turn sends efferent signals out to the immune system to dampen the responses. Such circuits provide control precision and integration not possible with diffuse, humoral control systems. Thus, the innate immune system is both the origin of signals that are converted to action potentials in the sensory arc, and it is the target of signals descending in the motor arc (*5*).

We have learned much about the efferent pathways controlling innate immunity, and there is now great interest in understanding more about how inflammatory and injurious factors activate the afferent input into this immunological and neurological system. Understanding these mechanisms as a function of "top-down" neurological regulatory processes—that is, as immune responses that are the result of action potentials originating in neurons—should stimulate the identification of new molecular targets and the development of therapeutic alternatives. From worms to humans, there is a consistent evolutionary theme that the immune system detects changes in the environment, and its actions modify the behavior of the animal. The loop is closed by reflex signals originating in the nervous system that modify innate immune responses to maintain homeostasis.

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CHEMISTRY

Designing the Next Generation of Chemical Separation Membranes

New materials can be prepared as membranes that may allow their performance to beat long-standing limits.

Douglas L. Gin and Richard D. Noble

Synthetic membranes are used in many separation processes, from industrial-scale ones—such as separating atmospheric gases for medical and industrial use, and removing salt from seawater—to smaller-scale processes in chemical synthesis and purification. Membranes are commonly solid materials, such as polymers, that have good mechanical stability and can be readily processed into high–surface area, defect-free, thin films. These features are critical for obtaining not only good chemical separation but also high throughput. Membrane-based chemical separations can have advantages over other methods—they can take less energy than distillation or liquefaction, use less space than absorbent materials, and operate in a continuous mode. In some cases, such as CO_2 separations for CO_2 capture, their performance must be improved. We discuss how membranes work, and some notable new approaches for improving their performance.

Membranes work by forming a barrier between two phases (e.g., salt water and fresh water) that restricts the movement of some molecules while letting others through (*1*). Separation is driven by a difference in concentration or pressure (or both) across the membrane—pressurization is the main energy input. Membranes are either dense or porous, depending on how the molecules move across the barrier. In dense membranes, molecules dissolve into the material and diffuse through it (*1*). The product of a molecule's solubility and diffusivity is its perme-

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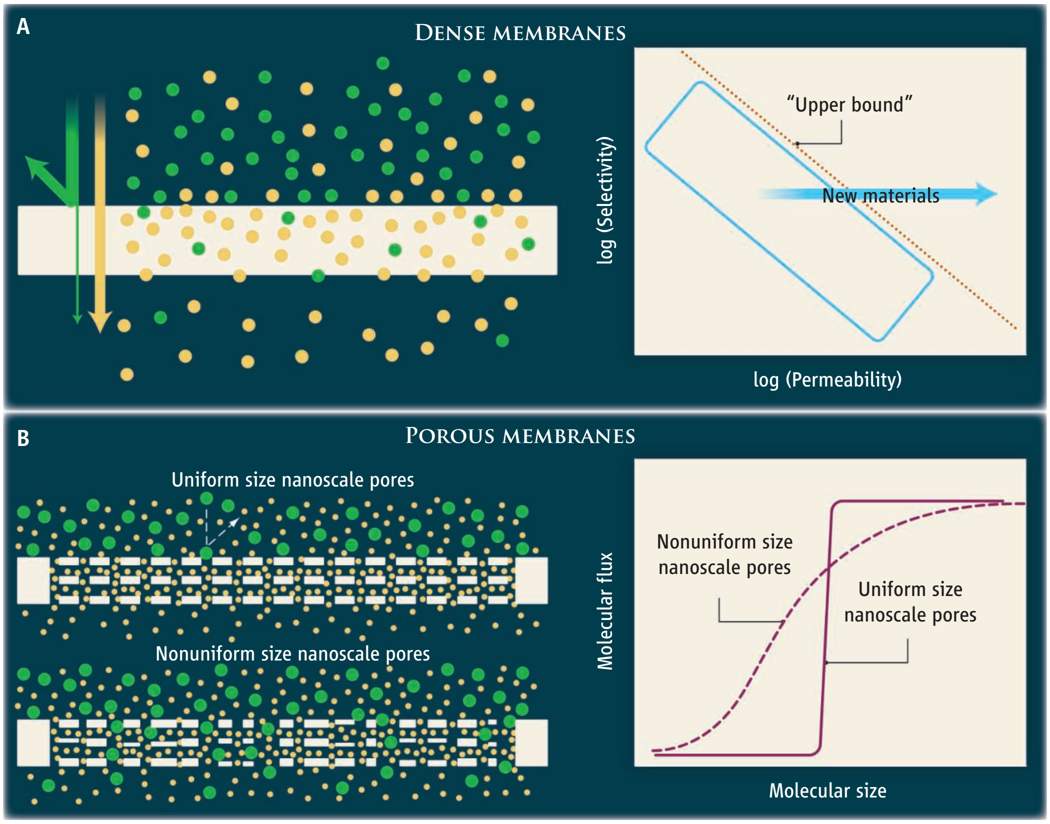

Chemical separation with dense and porous membranes. **(A)** For dense membranes, orange and green molecules move through the membranes at different rates because they have different permeabilities *P*. The Robeson plot shows that conventional dense membranes separate mainly via differences in diffusivity, and performance is limited by an "upper bound." **(B)** Nanoporous membranes separate via molecular size differences. The examples shown are for pores that interconnect into a 3D network. With uniform pore sizes, it is possible to get complete separation (smaller molecules pass through—they have a higher molecular flux; larger ones are completely blocked). With nonuniform pores, the largest pore sizes (i.e., a distribution) dictate the selectivity, and both molecules can pass through.

ability *P*, and membranes are designed so that two (or more) molecules have different *P* values (see the figure, panel A).

In contrast, porous membranes for chemical separations should have pores that are ideally the size of single small molecules (≤1 nm), and molecules pass through as a gas or a liquid solution. Molecules can be separated by size because the nanopores act as a screen or sieve (*1*). Uniform nanopores with the correct size must be continuous across the membrane. If there is a distribution of pore sizes, most of the molecules will pass through the largest pores first (path of least resistance), thereby compromising selectivity (see the figure, panel B).

The limitation of conventional dense polymer membranes is best illustrated by gas separations. Differences in *P* mainly arise from diffusion differences of each gas component in the polymer film—solubilities tend to be similar. Materials that are more permeable (i.e., that have higher throughput and would process gas faster) also have a more open structure and thus have lower selectivity. This compromise leads to an upper bound for separation performance that is shown graphically by plots generated by Robeson (*2*).

A new approach in the design of dense membranes is to use room-temperature ionic liquids (RTILs) in various morphologies. RTILs are liquid-phase organic salts (i.e., ionic compounds) with negligible vapor pressure (avoiding evaporation losses), high thermal stability, and intrinsic solubility for certain gases. Unlike conventional polymers, RTILs perform gas separations via solubility differences. They have been applied to CO_2 separations, but the wide variety of RTILs allows for many candidate separations. Also, RTIL derivatives can be prepared that allow the molecules to be polymerized to form solids so that membranes can be prepared in various morphologies, such as films (*3*), solid composite structures with RTIL within the structure (*3*), and gels (*4*). For RTIL morphologies, the limit on a Robeson plot is determined by the performance of the liquid itself as a membrane because the other morphologies have the same solubility selectivity but different diffusion rates.

Poly(RTIL) films have recently been tested for gas separations up to 40 atm pressure for mixtures of CO_2 and CH_4. The conditioning or morphology change caused by the incorporation of gases such as CO_2 at these high pressures is reversible compared to conventional polymers that exhibit irreversible conditioning at these pressures (*5*). Examples of improved separations include CO_2 from N_2 for postcombustion cleanup of flue gas from power plants.

For nanoporous membranes, several methods have recently been developed that afford materials with uniform molecular-size pores. For example, deposition techniques have been successfully used to reduce the pore size of commercial nanoporous polymer and ceramic membranes down to molecular dimensions (*6*). Recent advances in blending organic polymers with inorganic zeolites have afforded viable composite membranes with uniform pore sizes in the 0.3- to 0.7-nm range for light gas separations, such as CO_2, N_2, and CH_4 (*7*).

Similar approaches for making polymer-based composite membranes containing metal-organic framework compounds (*8*), carbon nanotubes (*9*), and peptide nanotubes (*10*) as the porous component have also been found to be promising for separating different-size ions in water and mixtures of light gases. "Molecular square" coordination compounds (*11*) and macrocyclic surfactants (*12*) also form membranes with molecular-size pores when applied as ordered thin layers on membrane supports. Ordered surfactant liquid crystal assemblies formed in water have successfully been polymerized into membranes with three-dimensional (3D) interconnected pores, smaller than 1 nm in diameter, that act as molecular sieves for water desalination (*13*). Selectively etched phase-segregated block copolymers (*14*) and colloidal crystal assemblies (*15*) are two promising platforms with uniform pores in the 10- to 100-nm range. Such materials are useful for macromolecular or protein separations, but methods are needed to bring the pore sizes down to molecular dimensions if they are to be useful for small-molecule separations.

Other factors are also important for making practical membranes with high throughput, 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.

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APPLIED PHYSICS

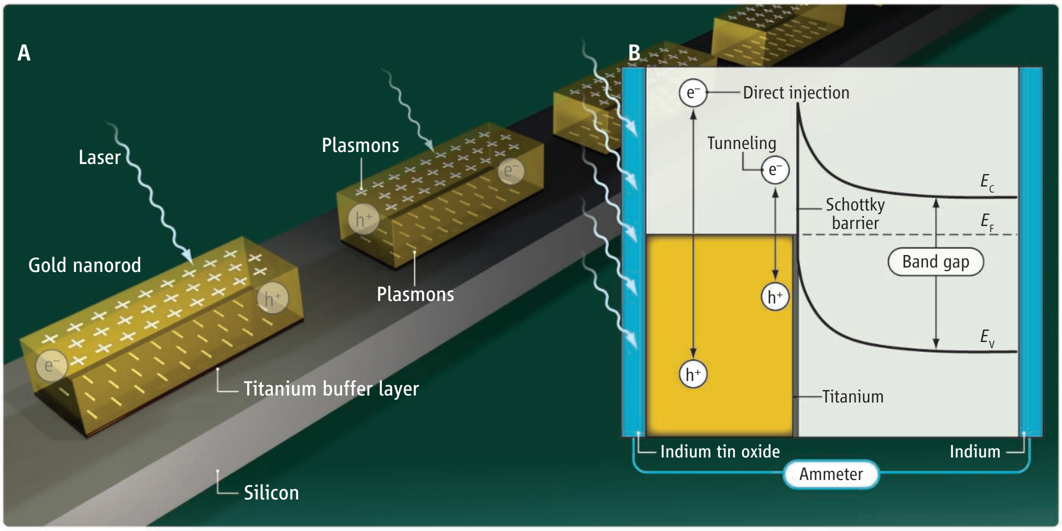
Hot Electrons Cross Boundaries

Martin Moskovits

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

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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