MATERIALS SCIENCE

Making High-Flux Membranes with Carbon Nanotubes

Separation of gases and liquids into their constituents is crucial for many industrial processes. Membranes that incorporate nanotubes show promise for high selectivity and throughput.

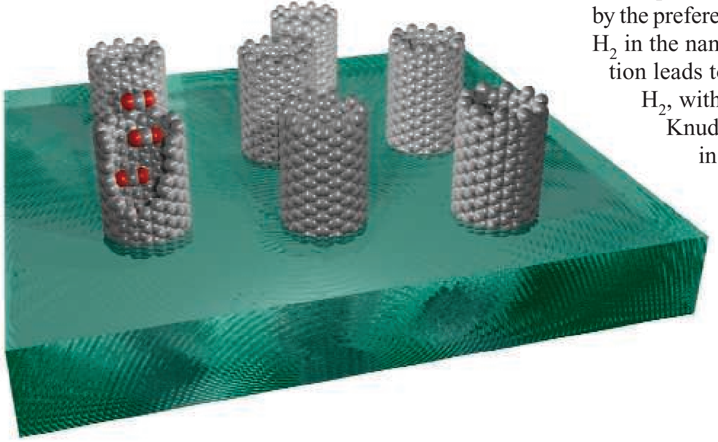
David S. Sholl and J. Karl Johnson

In 1871, James Clerk Maxwell devised a thought experiment whereby a “demon” separates molecules without performing work. The practical realization of such a demon would be extraordinarily useful, because at present, vast amounts of energy and money are expended around the globe separating chemical mixtures. Even separation of very simple molecules can have enormous implications. For example, purifying O_2 and N_2 from air is a multibillion dollar industry, and the ability to economically separate CO_2 from power plant flue gases could revolutionize efforts to reduce greenhouse gas emissions. Efficient membranes are real-world analogs of Maxwell’s demons that can separate chemicals with little (although never zero) work. On page 1034 of this issue, Holt and co-workers (*1*) describe experiments that are a fascinating step toward the development of highly efficient membranes.

The separation of gases and liquids by membranes can often be more cost and energy effective than traditional separation methods, such as distillation or absorption. An ideal membrane would have excellent stability under a wide range of process conditions, high selectivity for the chemicals of interest, and also produce a large molecular flux with a small driving force. Most membranes in use industrially are polymeric, and the fabrication of these devices is highly developed. Polymeric membranes for gas separations show a near-universal tradeoff between flux and selectivity (*2*); materials with high throughput also have low selectivity, and vice versa. Polymeric membranes are also typically unsuitable for very high–temperature applications. New membrane materials that can overcome these fundamental hurdles could ultimately drastically reduce the energy consumed in present-day separation operations.

The possibility of using carbon nanotubes as membranes for gas separation has been recognized for some time. The first examinations of this idea used molecular dynamics (MD) simulations of gas transport inside single-walled nanotubes (*3*, *4*). These simulations predicted that the transport of gases inside nanotubes is orders of magnitude faster than in any other known materials with nanometer-scale pores. These rapid transport rates exist because the walls of nanotubes are much smoother (on atomic scales) than other materials.

These model predictions have now been tested experimentally by Holt *et al.*, who have fabricated the first membranes from aligned single- and double-walled nanotubes. This work follows similar experiments by Hinds and co-workers with membranes made from multiwalled nanotubes (*5*, *6*). Both groups fabricated membranes in multistep processes, with the end result being nanotubes that penetrate a thin impermeable film (see the figure); Holt *et al.* used a silicon nitride matrix whereas Hinds *et al.* used a polymer. The pore diameters of nanotubes in the membranes made by Holt *et al.* are 1.3 to 2 nm, whereas the nanotubes used by Hinds *et al.* are considerably wider. Experimental observations of single-component gases permeating through both types of membranes show rapid transport of gases. The transport rates observed by Holt *et al.* for a range of gases are one to two orders of magnitude larger than would be predicted by assuming a Knudsen description, which is in quantitative agreement with predictions from simulations (*7*).



Faster flow. A schematic illustration of a membrane in which single-walled carbon nanotubes (gray) create avenues for transport of molecules (shown as red and gray balls passing through a nanotube) across an otherwise impermeable film (green).

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These experiments show that carbon nanotube membranes can have spectacularly high fluxes, but to be useful as membranes, they must also show high selectivity. The experiments to date have only examined single-component transport, so no direct information on this crucial issue is available. As is commonly the case for nanoporous membranes, estimation of membrane selectivities from single-component experiments is not expected to be accurate. Mixture selectivity has been studied with MD simulations of single-walled nanotube membranes for CH_4/H_2 mixtures (*8*), which predict that the selectivity is dominated by the preferential adsorption of CH_4 relative to H_2 in the nanotubes. This preferential adsorption leads to selective transport of CH_4 over H_2, with selectivities as high as 10 to 20. Knudsen transport of this gas mixture, in contrast, would give a selectivity of 2.8, favoring H_2 transport over CH_4.

The discussion above has focused on gas separations, but the need for efficient liquid separations is just as great. Both Holt *et al.* and Hinds and co-workers have performed experiments assessing water transport through their nanotube membranes. Similar to what is seen with gases, water is observed to move through the membranes extremely rapidly. The transport rates reported by Holt *et al.* are in good agreement with predictions made from MD simulations (*9*). Experimental studies of the selectivity of these membranes when they are applied to liquid mixtures will be of great interest.

The path to move from the elegant membranes fabricated by Holt *et al.* and Hinds *et al.* to devices suitable for large-scale applications—for example, CO_2 capture—will not be an easy one. The key challenge in this context is to scale up the fabrication techniques that have now been successfully demonstrated to economically produce membranes with large surface areas. The scope of this challenge is large, but the potential payoff is commensurately large. These experiments should also motivate other approaches to membrane fabrication that use carbon nanotubes as one component in a composite membrane rather than as the sole avenue for molecular transport across a membrane. So-called mixed matrix membranes that embed small nonpolymeric parti-

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cles inside a polymeric matrix are a well-known route to improving the properties of polymeric membranes (*10*). Mixed matrix membranes hold a great economic advantage over "pure" inorganic membranes, because the inclusion of the inorganic component is, in principle, a relatively simple addition to existing methods for making large–surface area polymeric membranes. The experiments of Holt *et al*. strongly suggest that mixed matrix nanotube/polymer membranes may bring us closer to mass production of devices that do the job assigned to Maxwell's fictional demon.

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CHEMISTRY

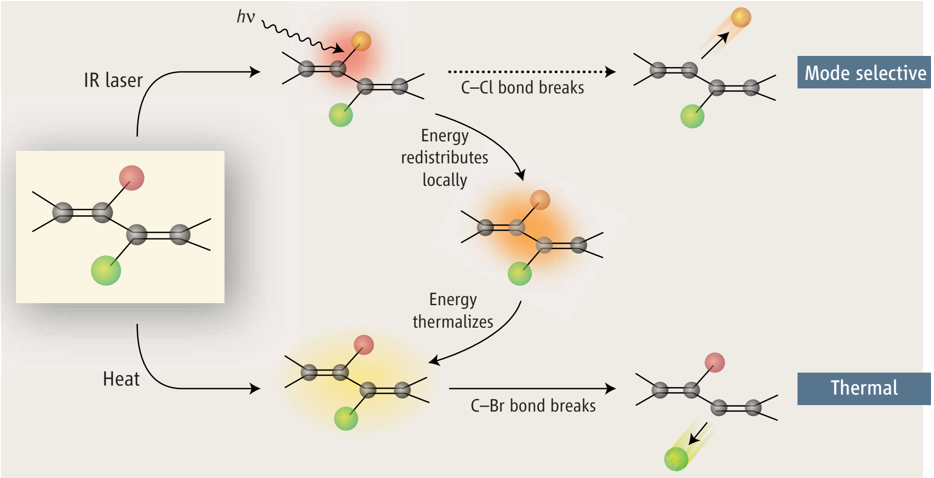
Mode-Selective Control of Surface Reactions

Researchers have achieved the goal of controlling chemical reactions by selectively exciting a single vibrational mode. A free-electron laser selectively desorbs H_2 from a silicon surface coated with hydrogen and deuterium.

John C. Tully

Mode-selective chemistry—the ability to energize a specific chemical bond and thereby promote a desired reaction pathway—has been a widely pursued goal. The vision of using a tunable infrared (IR) laser to divert a reaction from its dominant thermal pathway toward a desired product has even attracted commercial interest. For the most part, however, molecules have not cooperated. On page 1024 of this issue, Liu *et al*. (*1*) report convincing evidence for the mode-selective desorption of H_2 from a hydrogen-covered silicon surface.

The main impediment to IR mode-selective chemistry is that vibrational energy tends to be redistributed rapidly within a molecule. An initially excited, high-frequency localized mode can quickly de-excite by transferring its energy into combinations of lower frequency modes. In small molecules with sparse vibrational modes, few (if any) combinations of low-frequency modes can accept the energy, and the lifetime of the initially excited mode may be sufficiently long to allow mode-selective chemistry. Indeed, the outcome of the gas-phase reaction of H atoms with singly deuterated water (HOD) can be controlled through laser excitation of specific HOD vibrational modes (*2*, *3*). However, in large molecules, in condensed phases, and at surfaces, huge numbers of low-frequency modes can accept energy, and energy randomization is very rapid (generally on the picosecond time scale or faster). Thus, energy does not remain localized in a bond for a sufficiently long time to influence a chemical reaction. The resulting chemistry is thermal rather than selective: the weakest bond breaks or the most reactive site reacts (see the figure).



Conventional wisdom. The hypothetical molecular fragment shown here contains a weak bond between bromine (green) and carbon (gray) and a stronger bond between chlorine (red) and carbon. Heating results in thermal cleavage of the weakest bond, C–Br. IR excitation of the C–Cl vibration aims to selectively break this stronger bond. However, rapid intramolecular redistribution of the laser energy is likely, producing the same result as heating: the nonselective breaking of the weaker bond. The experiments of Liu *et al.* are more complex than this illustration, but nevertheless demonstrate a mode-selective, nonthermal pathway.

Attempts at IR mode-selective desorption of molecules from surfaces have been reported previously, but none have convincingly shown selectivity. A beautiful series of experiments was carried out by T. J. Chuang and co-workers in the early 1980s. In one example (*4*), they observed greatly enhanced desorption yields of NH_3 from copper and silver surfaces when the IR laser was tuned to resonance with an ammonia vibrational mode. However, when they co-adsorbed NH_3 and ND_3 on the surface and tuned the laser to an NH_3 vibrational frequency, both NH_3 and ND_3 desorbed in statistical (nonselective) proportions; NH_3 did not desorb preferentially. Thus, energy is deposited only when the laser frequency is resonant with a vibration, but the energy rapidly randomizes, and the subsequent chemistry is driven by nonselective heating. Redlich *et al*. recently reported similar findings for isotopic mixtures of methane physisorbed on an NaCl surface; again, isotopes were found to desorb in statistical proportions irrespective of which isotope was vibrationally excited (*5*).

The experimental findings of Liu *et al*. (*1*) are in striking contrast with the wavelength-dependent but nonselective desorption found in these previous studies. The authors first created an adsorbed layer of about 15% H atoms and 85% D atoms on an Si(111) surface. They then irradiated the surface with a free-electron laser tuned to the 4.8-μm Si-H stretching mode. They found that almost all desorbing atoms were H_2; less than 5% of desorbing molecules were HD or D_2. This startling result rules out any local heating mechanism, which would produce a statistical mixture (2% H_2, 26% HD, and 72% D_2). Liu *et al*. have thus clearly

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