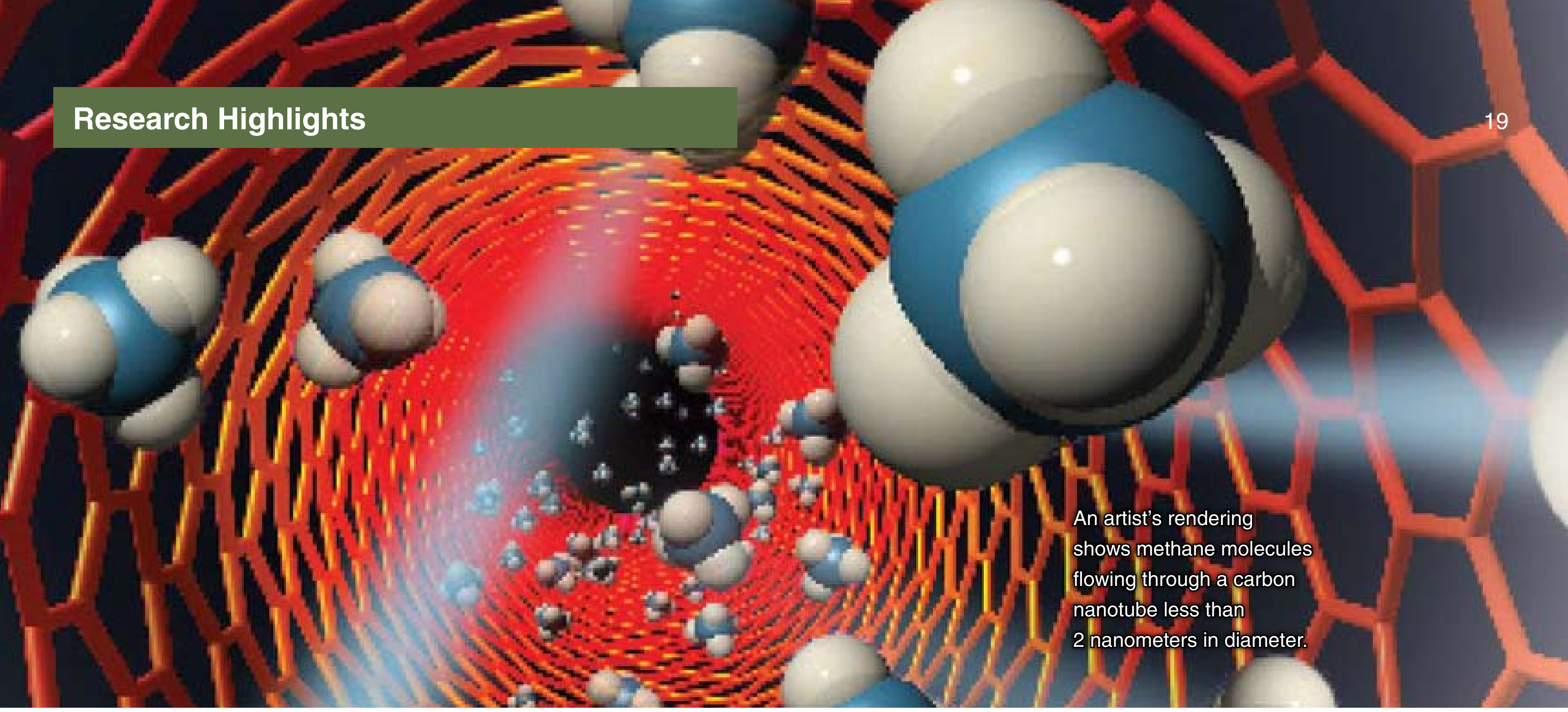

An artist's rendering shows methane molecules flowing through a carbon nanotube less than 2 nanometers in diameter.

Tiny Tubes Make the Flow Go

IMAGINE a garden hose that can deliver as much water in the same amount of time as a fire hose 10 times larger. You've entered the realm of carbon nanotubes, where flow rates are enhanced many times over.

These tiny tubes have extremely smooth interior walls that allow liquids and gases to rapidly flow through them, while their tiny pore diameters block larger molecules. A Livermore team led by physicist Olgica Bakajin and chemist Aleksandr Noy has created a membrane with millions of carbon nanotubes—each 50,000 times thinner than a human hair—aligned on a silicon chip. Carbon nanotube membranes offer some enticing possible uses, ranging from a more energy-efficient method to filter salt from seawater to dialysis applications.

The principal contributors to the work are staff scientist Jason Holt (a former postdoctoral researcher) and Hyung Gyu Park, a participant in the Student Employee Graduate Research Fellowship (SEGRF) Program. Other Laboratory team members include staff scientist Yinmin Wang, postdoctoral researcher Michael Stadermann, and SEGRF participant Alexander Artyukhin. The team collaborated with Costas P. Grigoropoulos, a professor at the University of California at Berkeley.

Making Nanotube Fast Flow a Reality

Carbon nanotube membranes were first modeled in computer simulations. Only recently has the technology been developed to to study their behavior in experiments. "A number of molecular dynamics simulations have appeared in the literature over the years, predicting fast transport of gases and fluids in very small nanotubes," says Noy. "However, no physical experiments had been performed to prove or disprove flow-rate predictions. Here, at Livermore, we had the people, facilities, expertise, and resources to explore this phenomenon."

With funding from Livermore's Laboratory Directed Research and Development Program and support from the Chemistry, Materials, and Life Sciences Directorate, the team tackled the task of creating an array of carbon nanotubes. One challenge was to develop a method for growing nanotubes with one or, at most, two walls. "Previously, the only nanotubes grown had four to six layers of walls," says Noy. With so many walls, the possibility was high that at least one tube layer would flop over when growing and form a cap, sealing the pore.

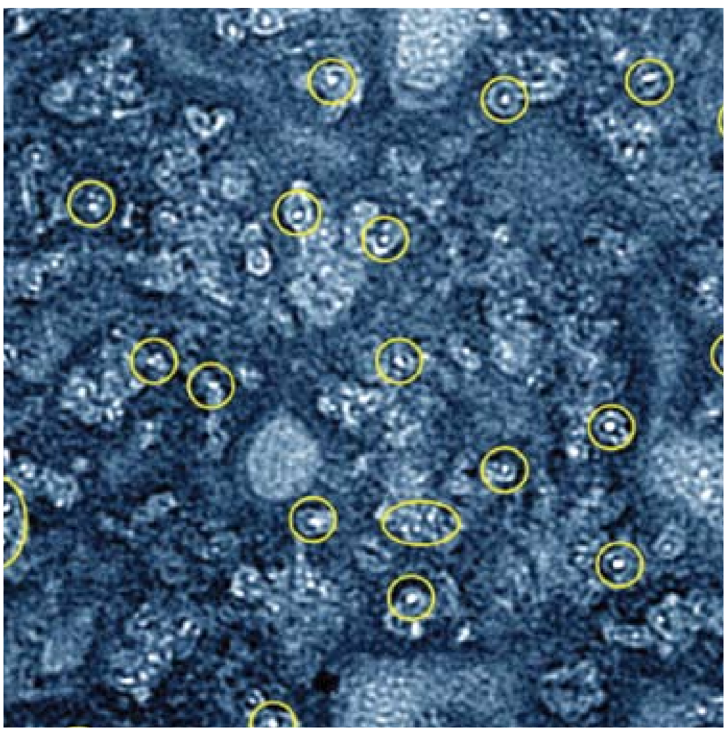
The team successfully grew nanotubes just one or two walls thick that had a more likely chance of remaining open. Nanotubes with fewer walls also have the benefit of smaller pore sizes, allowing them to filter out even smaller molecules. Multiwalled nanotubes have pores ranging from 5 to 10 nanometers in diameter, but double-walled tubes have pores measuring just 1 to 2 nanometers in diameter—about the width of six water molecules.

To create these membranes, the team developed a fabrication process compatible with microelectromechanical systems. The process uses catalytic chemical vapor deposition to grow a dense "forest" of double-walled tubes on the surface of a silicon chip. The next challenge was to fill the gaps between the nanotubes without leaving microcracks that would allow fluids or gases to seep through the membrane.

"We designed a deposition process that coats the outside walls of the tubes and the spaces between them with silicon nitride," explains Bakajin. Subsequent transmission electron microscopy images showed that this process produces gap-free membranes. The excess silicon nitride is removed from both sides of the membrane, and the ends of the nanotubes are re-opened with reactive ion etching. "The membranes are impermeable to both liquids and gases until this last etching step," says Bakajin.

The first time the scientists set up an experiment, they covered the top of the membrane with water in which 2-nanometer-diameter gold particles were suspended and then left the experiment overnight. "When we returned the next morning, we were surprised to find a small puddle on the floor under the membrane," says Park. Holt adds, "We at first thought the membrane had broken, but it evidently allowed the water through, while blocking the gold nanoparticles that were just a bit larger than the nanotube pores. The experiment was a success."

The team repeated the experiment several times using different membranes to verify the flow rates through the double-walled carbon nanotube membranes. The team calculated the flow rate per tube from the total flow through the membrane, assuming every tube remained open. The measured water flow was comparable to flow rates extrapolated from molecular dynamics simulations. Because at least some of the tubes were closed, the actual flow rate was higher than the calculated rate.



Transmission electron microscopy is used to capture a high-quality image of a carbon nanotube membrane. Several of the nanotubes are circled.

Tiny Tubes Have Big Applications

The Livermore team envisions many uses for such tiny membranes. One of the main applications is to purify, demineralize, and desalinate water. The worldwide need for simple, energy-efficient ways to produce clean water is urgent. Approximately 1 billion people do not have access to clean water. In addition, more than 2 billion people now live in water-stressed areas, a number that is expected to climb to 3.5 billion by 2025. Desalination—the process of removing salts and suspended solids from brackish water and seawater—is one way to alleviate this problem.

Membranes are key to a desalination process known as reverse osmosis, in which water is pushed through a semipermeable membrane that blocks dissolved salts. One drawback of this process is the amount of energy it requires. A typical seawater reverse-osmosis plant requires 1.5 to 2.5 kilowatt-hours of electricity to produce 1 cubic meter of fresh water. The unusually fast flow rates of water through the carbon nanotubes are thus encouraging. If the tiny nanotubes created at Livermore could be scaled up and designed to exclude salts, they could enable desalination facilities to sharply reduce the amount of energy needed to purify water. In much the same way, nanotubes could also someday be used in kidney dialysis to filter waste products such as potassium, acid, and urea from blood.

The team's research also has the potential to enhance fundamental knowledge of how fluids and gases flow at extremely tiny scales. Such understanding could impact the design of microfluidic chips now under development for genetic analysis. It could also elucidate how ions and water flow through cellular pores.

"Our nanoscale experiments have given us insight into unique and useful material properties," said Noy. "The unusually fast flows that were predicted in simulations have now been proven experimentally. The reality of this phenomenon opens a number of doors."

Bakajin adds, "We succeeded in exploring this newly discovered phenomenon as well as we did because of the resources at the Laboratory: the capability for in-house nanotube synthesis that was pivotal for the development of the double-walled nanotube arrays, the Center for Micro- and Nanotechnology's clean room facility, and most importantly, the people who joined the team. These people, with their skills, expertise, and enthusiasm, and their willingness to come together and find ways to combine their narrow specialties into something new and never seen before, made the project succeed."

—Ann Parker

Key Words: carbon nanotube membrane, Center for Micro- and Nanotechnology, filtration, microfluidics.

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