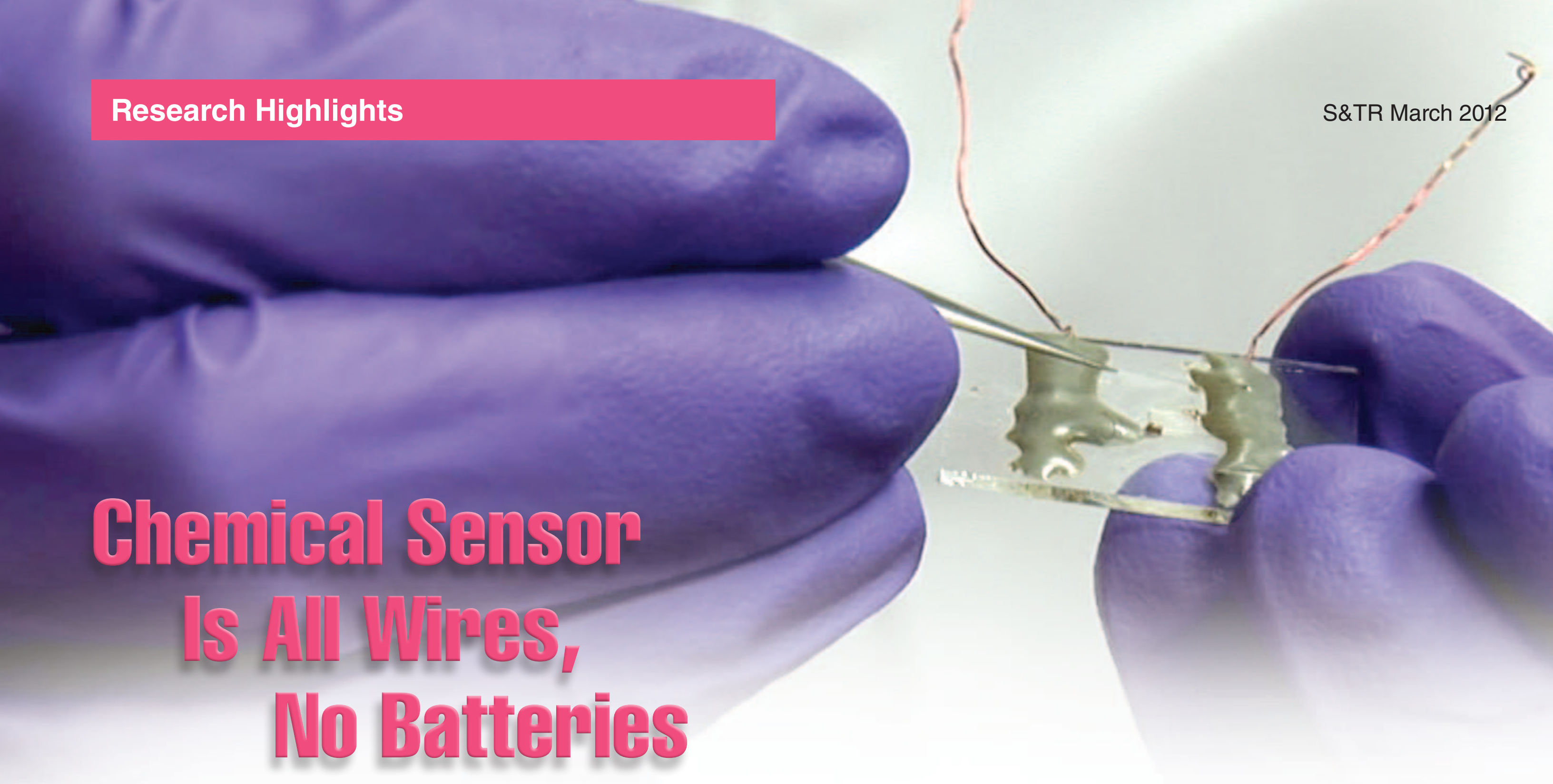


Chemical Sensor Is All Wires, No Batteries

The batteryless nanowire sensor is sensitive, fast, and small—about 2 millimeters long—and could be the basis of a small-scale handheld chemical detector.

SENSOR technology keeps advancing with the development of smaller and smaller sensors that have higher and higher sensitivities. However, when it comes to conventional chemical detectors, most (if not all) still require a power source, that is, a battery, and therein lies a challenge. Battery-powered sensors require regular maintenance and replacement, making them problematic for field use. And, with sensors shrinking in size, the power source is often larger than the sensor itself, which defeats the purpose of miniaturization.

Fortunately, Livermore materials scientist Morris Wang and colleagues have found a way to bypass the power source requirement. Their "batteryless" nanosensor can identify different chemical species in less than a second, giving it potential for homeland security and medical applications.

Scientific Serendipity at Work

Wang and former colleague Xianying Wang (a visiting scientist from the University of Shanghai for Science and Technology) stumbled across the batteryless nature of nanowires while conducting tests for energy conversion applications. The scientists had embedded zinc-oxide (ZnO) nanowires in a polymer responsive to environmental conditions such as humidity and temperature. Changing conditions cause the polymer to swell or shrink, which in turn puts a force on the nanowires. Because the ZnO nanowires are piezoelectric, applying a force induces a voltage in the wires. On this particular day, the scientists were dripping solvents on the polymer to make it swell and stretch the nanowires. After applying ethanol, they saw an unexpected voltage spike—a far greater blip than the swelling mechanism would cause.

On seeing the strong signal, Livermore's Wang thought something odd might be going on. He explains, "I always tell my postdocs that getting unusual, unexpected, or abnormal experimental results can often be a very good thing. It may mean they have discovered something new. The weirder the results, the more exciting they may be. In this particular case, we had a very weird result." Upon further examination, they discovered that the nanowires—which poke out of the polymer base like teeny fingers—were interacting directly with the alcohol molecule.

From Alcohol to TNT

Using specialized Livermore facilities—including the Engineering Directorate's Center for Micro- and Nanotechnology and the Physical and Life Sciences Directorate's Nanoscale Synthesis and Characterization Laboratory—the team fabricated and tested two different platforms to verify their initial discovery. The first platform was fabricated from single-crystalline, vertically aligned ZnO nanowires. The second platform used silicon (Si) nanowires in a random tangle. "Zinc-oxide and silicon have proved to be good sensor materials," says Wang.

In the first platform, the 6- to 7-micrometer-long ZnO nanowires were infiltrated with a polyvinyl chloride polymer and etched with oxygen plasma, leaving exposed "fingers" about 0.1 to 0.5 micrometers tall. For the sensing experiments, a gold–titanium film and silver paste were used to make the top and bottom electrical contacts. The scientists then monitored the change in electric potential on the two ends of the nanowire.

The second platform used randomly aligned Si nanowires up to tens of micrometers long. About 80 percent of the nanowire tangle was sealed with polymer, leaving the remaining 20 percent exposed. Gold–titanium film was evaporated on two opposite sides of the substrate as electrical contacts. In this system, scientists monitored the change in electrical potential between the exposed and unexposed nanowires.

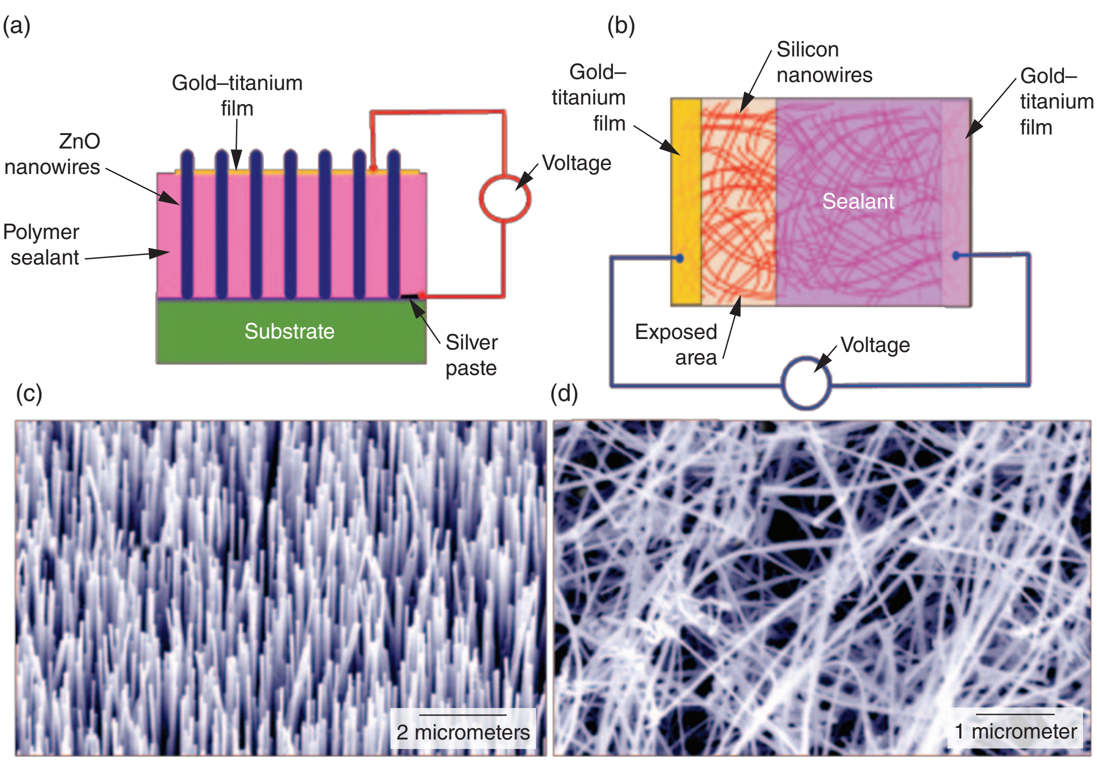
The team experimented with more than 15 different organic solvents, including acetone, chloroform, toluene, and ethanol, by dripping each chemical onto a sensor at room temperature. With ethanol, for example, the electric voltage rose sharply, peaking at approximately 170 millivolts. The signal rise was almost instantaneous and decayed slowly to zero as the ethanol evaporated. Other solvents produced different characteristic signals, yielding voltage "fingerprints" for each substance.

Wang then worked with engineer Chris Spadaccini in the Center for Micro- and Nanotechnology to test the nanowire device on explosives such as TNT (trinitrotoluene) and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane). The results were very encouraging. The sensor was able to distinguish between different types of chemical explosives, which offers many new possibilities. "The device is potentially very sensitive and fast," says Spadaccini. "In addition, because it is so small, it could be easily integrated into a handheld system." Alex Hamza, director of the Nanoscale Synthesis and Characterization Laboratory, also sees the future benefits of batteryless technology, adding, "Developing techniques to power sensors and other nanostructured devices is vitally important to furthering their widespread use."

How It Happens

The nanosensors take advantage of a unique interaction between a chemical species and the surface of a semiconductor nanowire. The interaction stimulates an electric charge between the two ends of the exposed, vertically aligned ZnO nanowires or between the exposed surfaces of a Si tangle. When chemical molecules attach to surface molecules of the nanowire, they induce a change in the charge distribution (density of the electrical charge) on the nanowire surface. This change produces a voltage between the ends of the nanowires, generating a measurable electric signal.

To better understand what was happening at the atomic level, Wang turned to physicists Daniel Aberg and Paul Erhart in the Physical and Life Sciences Directorate. Aberg and Erhart focused on the chemisorption effects of the ethanol molecule to look for an

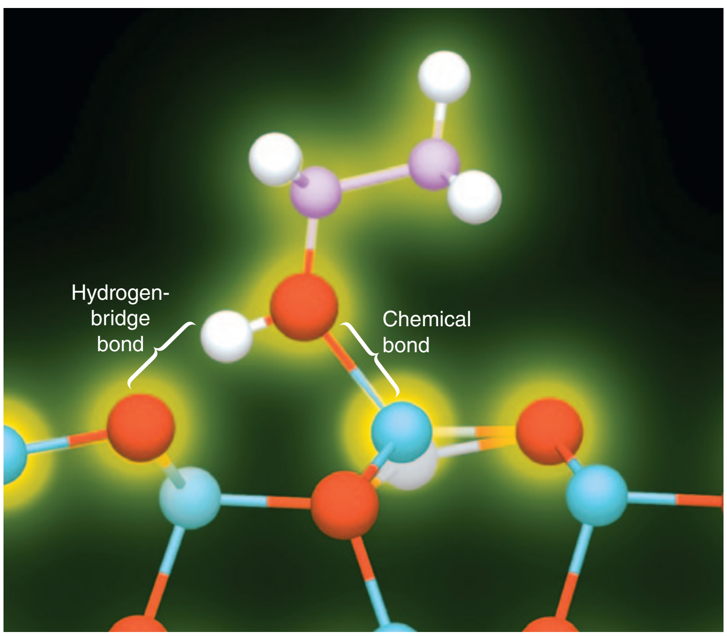


Chemical sensor designs use (a) zinc-oxide (ZnO) nanowires aligned vertically in a polymer sealant and (b) silicon nanowires in a tangled, randomly aligned formation, partially in sealant. Scanning electron micrographs show (c) ZnO nanowires and (d) a silicon nanowire tangle. In each system, chemical molecules cause changes in the charge distribution of the nanowire surface, producing a detectable electrical signal.

explanation. In chemisorption, a chemical coats an exposed surface of a material, and the chemical and surface molecules create new electronic bonds. This process results in a new chemical species that forms a thin surface film, sometimes only one molecule thick. Corrosion and oxidation are two common products of the chemisorption process.

Aberg and Erhart used HERA, a large-capacity Linux cluster in Livermore's Open Computing Facility, to run quantum mechanical calculations on detailed interactions at the atomic level. Results from the calculations indicated that the ethanol molecule had a negative adsorption energy when interacting with the top or side surfaces of the ZnO molecule. Aberg and Erhart experimented with a dozen or so different positions before determining the lowest energy level for the system. In this state, the oxygen atom in ethanol bonds with a zinc atom in the nanowire. Another bond (a hydrogen-bridge bond) forms between a hydrogen atom in ethanol and an oxygen atom in the nanowire.

The researchers also found that the degree of detection sensitivity is linked to the polarity of the molecules involved. "Signal strength is directly tied to the dipole moment of the molecule," says Wang. Many molecules have a dipole moment, which is a function of the molecule's asymmetric electrical nature. Water, for example, has a negatively charged oxygen atom at one end and two positively charged hydrogen atoms at the other. As a result, water molecules have a different charge at each end, and thus a polarity, much like the negative and positive poles of a battery. When molecules with a given dipole moment attach to a surface created of molecules that also have a dipole moment, the attaching molecules bind in a preferred direction. "The strength of the signal is determined by the dipole moment of the attaching chemical species and the surface area of the nanowire," says Wang.



In the lowest energy configuration of ethanol on ZnO nanowires, a chemical bond forms between the oxygen (red) atom in ethanol and a zinc (blue) atom, and a hydrogen-bridge bond forms between a hydrogen atom (white) of ethanol and an oxygen atom of the ZnO molecule. Yellow halos indicate the electron density, which is a measure of the probability of an electron occupying an infinitesimal element of space surrounding any given point. (Violet dots indicate carbon atoms in the ethanol molecule.)

Charging Forward with Batteryless Nanowires

Work will continue on refining the structure's detection of chemicals in liquids and on other aspects of the device as well. Jianchao Ye from the University of Shanghai for Science and Technology is on a one-year assignment at Livermore to help further develop the nanowire sensor. Ye, whose Ph.D. studies focused on the microscale mechanical characterization of metallic glasses, will investigate the device's sensitivity to very small amounts of chemical species, probably down to the parts-per-million scale, and look for ways to improve sensitivity. "One possible approach is to increase the surface area exposed to the chemical," says Ye. He also will explore the selective detection of certain biomolecules, a process which may be possible with some surface modifications to the ZnO nanowires. Ultimately, this work may lead to miniaturized sensor devices that are energy efficient and ecofriendly. "The beauty of this research lies in discarding an external power source," Ye notes. "Also, because zinc-oxide nanowires possess both semiconducting and piezoelectric properties, we hope to develop a nanosystem that has both sensing and actuation functions."

Batteryless, small, fast, inexpensive, and simple, these nanosensors are on their way to "electrifying" the chemical sensor field. The sensors made the inside cover of *Advanced Materials* last year, and commercialization of the technology is a possibility. Born out of researchers' willingness to explore an out-of-place result from a different experiment, the batteryless chemical nanosensor is proof that it pays to heed scientific serendipity and see where the unexpected may lead.

—Ann Parker

Key Words: battery, batteryless, Center for Micro- and Nanotechnology, chemical detector, chemical sensor, homeland security, medicine, nanoscience, nanowire, power source, semiconductor.

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