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Nanotech Power

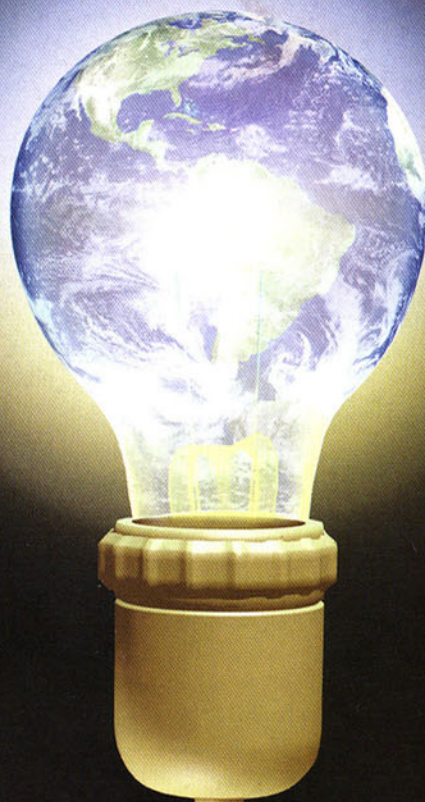
Tiny Devices
Reclaim Wasted Energy

Cancer Drug Paradox

It Kills Tumors by
Repairing Them

Sing Out!

The Physics
of the Voice



Self-Powered Nanotech

By Zhong Lin Wang

Nanosize machines need still tinier power plants

The watchmaker in the 1920s who devised the self-winding wristwatch was on to a great idea: mechanically harvesting energy from the wearer's moving arm and putting it to work rewinding the watch spring.

Today we are beginning to create extremely small energy harvesters that can supply electrical power to the tiny world of nanoscale devices, where things are measured in billionths of a meter. We call these power plants nanogenerators. The ability to make power on a minuscule scale allows us to think of implantable biosensors that can continuously monitor a patient's blood glucose level, or autonomous strain sensors for structures such as bridges, or environmental sensors for detecting toxins—all running without the need for replacement batteries. Energy sources are desperately needed for nanorobotics, microelectromechanical systems (MEMS), homeland security and even portable personal electronics. It is hard to imagine all the uses such infinitesimal generators may eventually find.

Researchers are pursuing several different routes toward power generation on a miniature scale. Options include exploiting random vibrations or motions (such as those near a roadway), temperature gradients (for example, ground temperature is fairly constant several meters below the surface), biochemistry, and external energy sources such as ultrasonic waves or even audible noises.

A key advantage of nanodevices and nanosystems is that they usually operate at a very low power level, in the range of nanowatts to microwatts, bringing nanogenerators for powering

them into the realm of the possible. Just think of the potential power sources a human body provides: mechanical energy, heat energy, vibration energy, chemical energy (in the form of glucose) and the hydraulic energy of the circulatory system. Converted into electricity, just a small fraction of this energy could be sufficient to power many types of small devices [see box on page 86].

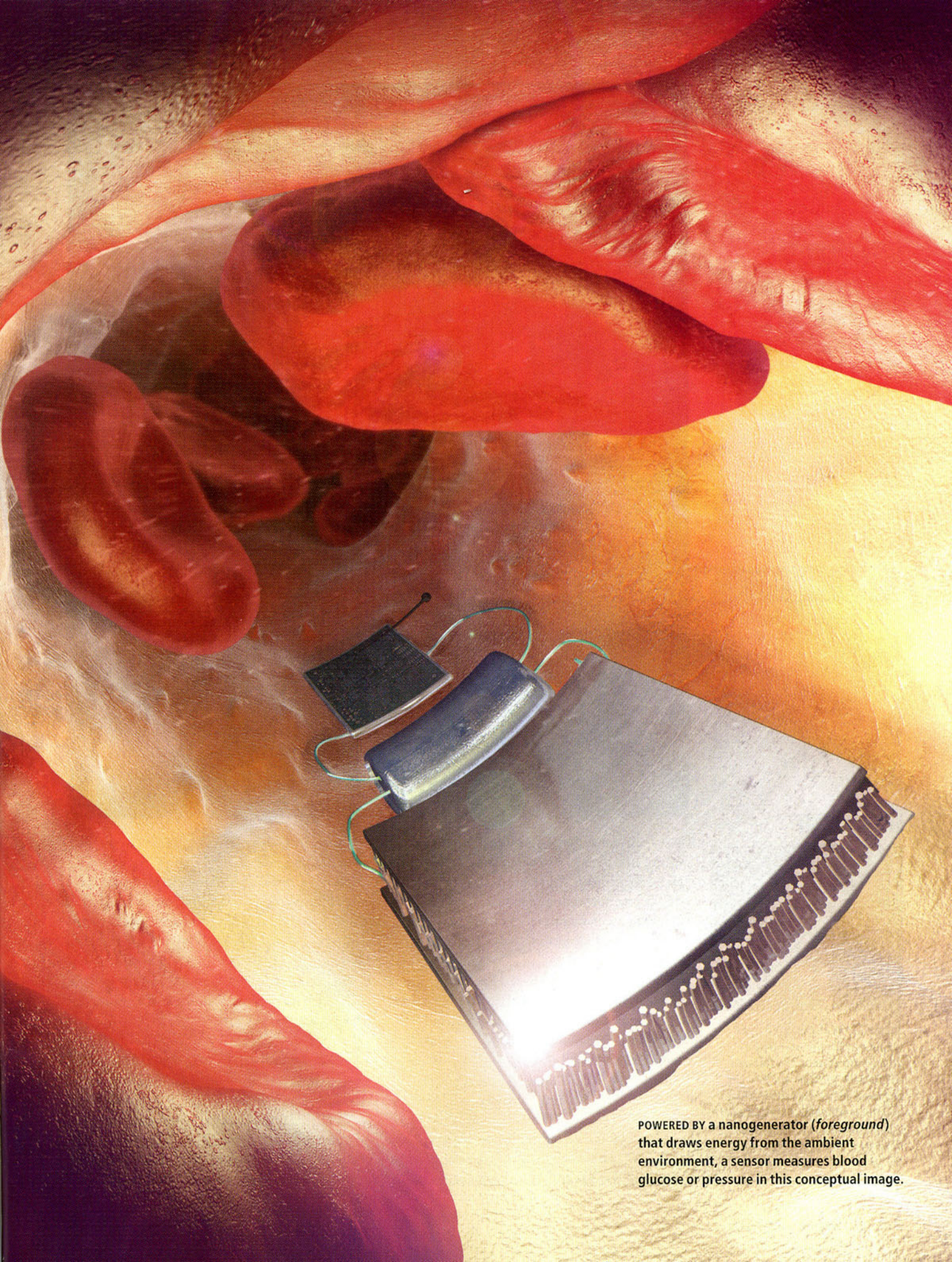
Power to the Tiny

Work on power generation for small devices has moved quickly since the late 1990s, when the proliferation of portable electronic gadgets attracted researchers to the problem of finding new ways to power them. Experimenters at the Massachusetts Institute of Technology's Media Lab, for example, devised an energy-scavenging shoe using the piezoelectric effect, whereby certain crystalline materials produce a voltage when mechanically stressed. But the difficulty of producing useful amounts of power soon drove scientists to explore generators that could meet the much smaller electrical power needs of MEMS. These silicon-based devices, whose dimensions are measured in microns (millionths of a meter) to millimeters (thousandths of a meter), have found many uses, including as accelerometers for automobile air-bag systems and as ink-jet printer nozzles. Biology and chemistry also offer opportunities for producing power [see box on page 87].

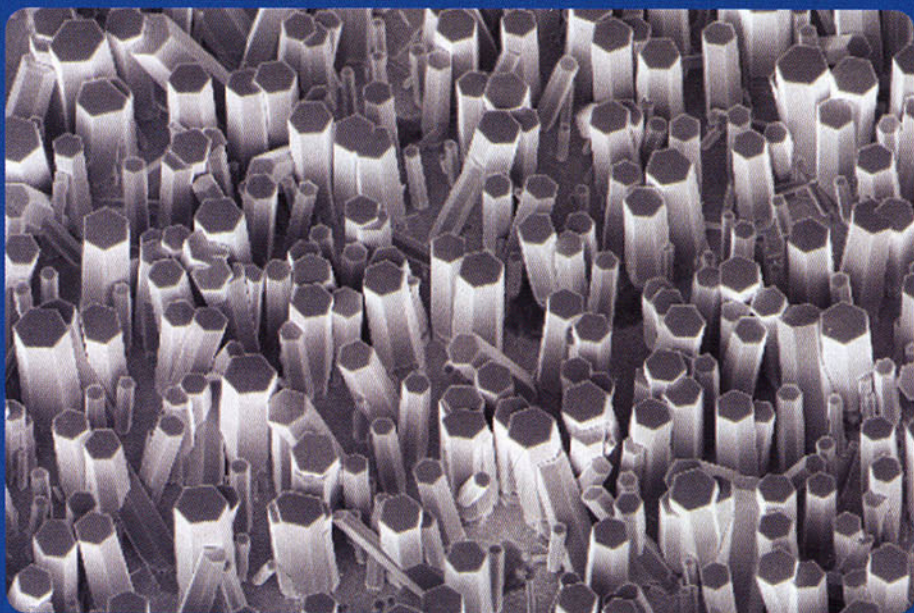
In recent years, scientists have built small vibration-based generators using both piezoelectric and electromagnetic transducers. The electromagnetic microgenerator utilizes a moving mag-

KEY CONCEPTS

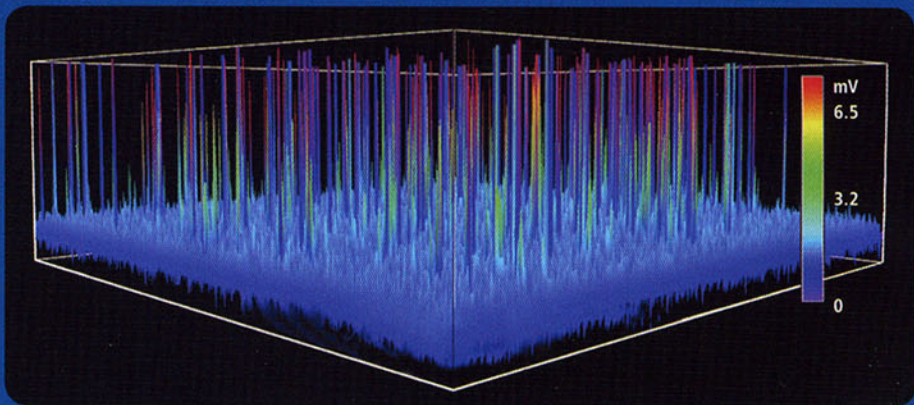
- Nanotechnology has huge potential—but those minuscule devices will need a power source that is better than a battery.
- Waste energy, in the form of vibrations or even the human pulse, could provide sufficient power to run such tiny gadgets.
- Arrays of piezoelectric nanowires could capture and transmit that waste energy to nanodevices.
- Medical devices will likely be a major application. A pacemaker's battery could be charged so it would not need replacing, or implanted wireless nanosensors could monitor blood glucose for diabetics. —The Editors



POWERED BY a nanogenerator (*foreground*) that draws energy from the ambient environment, a sensor measures blood glucose or pressure in this conceptual image.



ZINC OXIDE NANOWIRES, typically 30 to 100 nanometers in diameter and one to three microns in length, are seen in this scanning electron microscope image (*above*). The voltage output in millivolts of an array shows variability (*below*).



[THE AUTHOR]



Zhong Lin Wang is director of the Center for Nanostructure Characterization at the Georgia Institute of Technology. He discovered the nanobelt in 2000 and the world's smallest balance, the nanobalance, in 1998. Among his many honors, he received the 1999 Burton Medal of the Microscopy Society of America.

net or coil for inducing an alternating electric current in a circuit. Although some microgenerators have been fabricated at the scale of MEMS, the technology tends to require structures ranging from one to 75 cubic centimeters, which work in vibration ranges from 50 hertz (cycles per second) to five kilohertz. A typical piezoelectric vibration-based generator uses a two-layered beam of lead zirconium titanate, with a mass located at its unsupported end, somewhat like a swimmer poised at the end of a diving board. When gravity causes the beam to bend downward, the upper piezoelectric layer is under tensile strain and the lower layer is under compressive strain. The result is a positive and negative voltage across the beam. As the mass oscillates back and forth, an alternating voltage is created. But because this energy generator is

relatively large, gravity is important in driving its oscillating mass.

Now my research group at the Georgia Institute of Technology is working on piezoelectric power generation at the nanoscale. And at the nanoscale, things change. Gravity, which plays such a critical role in the larger world, is a very minor actor in the nanoworld as compared with the forces of chemical bonding and intermolecular attraction.

Where Gravity Doesn't Matter

The force of gravity is not available to us on a useful scale in the nanoworld. If one attempted to construct a piezoelectric generator with a nanometer-scale beam, gravity would make almost no contribution to sustaining the beam's motion, and the device would not work. There-

fore, we need another method to build a nanogenerator for powering autonomous devices. Our team has been exploring innovative nanotechnologies for converting mechanical energy (such as body movement and muscle stretching), vibration energy (such as acoustic and ultrasonic waves) and hydraulic energy (such as the flow of blood and other bodily fluids) into electric energy to power nanodevices.

My research focused on carbon nanotubes in the late 1990s. We invented a few techniques for measuring the mechanical, electrical and field-emission properties of individual carbon nanotubes using in situ microscopy. But we could not control a nanotube's electrical properties. I immediately realized that metal oxides are a new world—and why not explore those nanostructures? In 2000 I started with nanobelts, white woollike products made by baking a metal oxide such as zinc in the presence of argon gas at 900 to 1,200 degrees Celsius, and with nanowires.

Our research has become focused on aligned

zinc oxide nanowires, each of them a perfect six-sided, columnlike crystal that is grown on a solid conductive substrate using a standard vapor-liquid-solid process in a small tube furnace. We deposit gold nanoparticles, which serve as catalysts, on a sapphire substrate. An argon gas carrier flows through the furnace as a zinc oxide powder is heated. The nanowires then grow underneath the gold particles. The typical diameter of the nanowires is 30 to 100 nanometers, and they measure one to three microns in length.

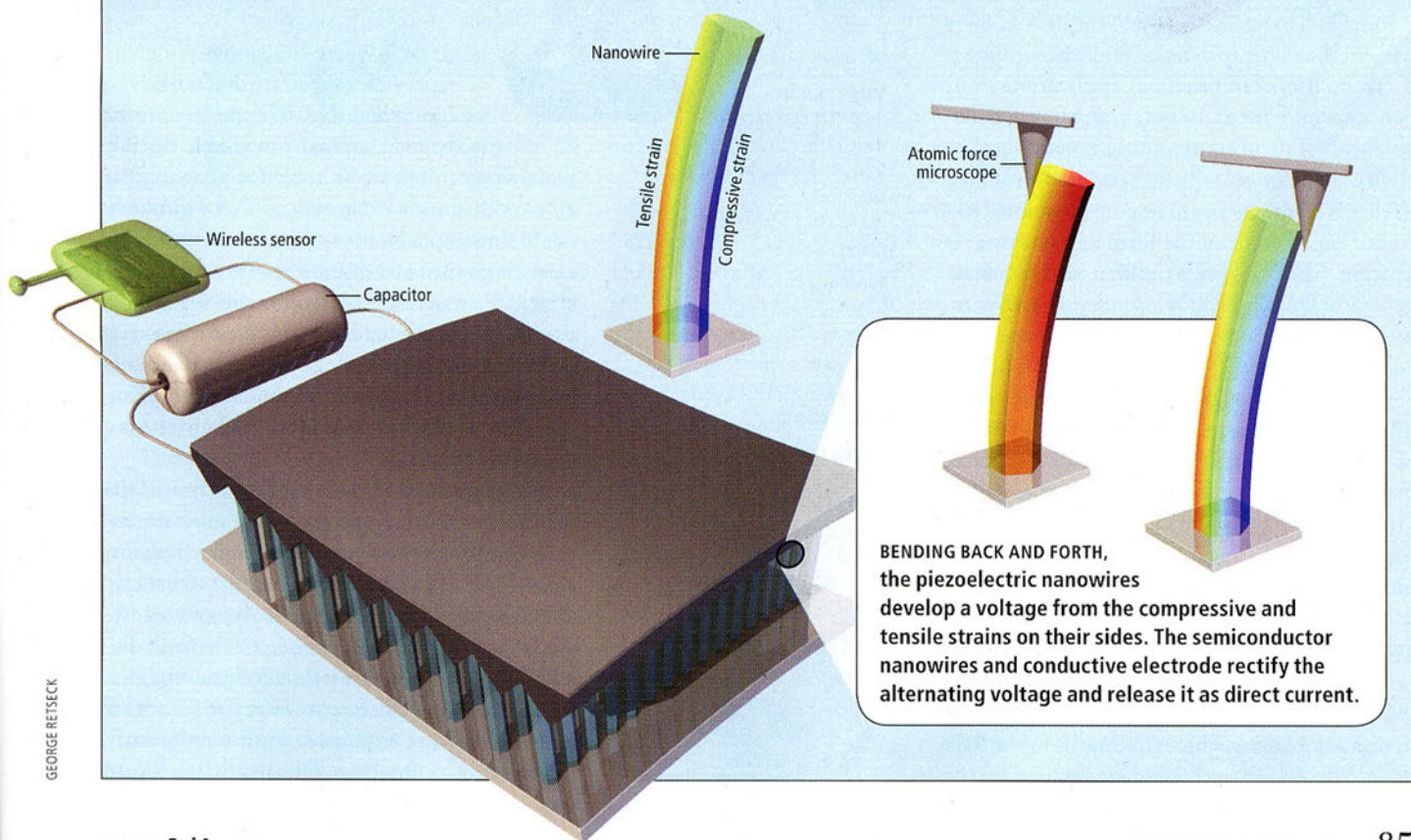
The idea of converting mechanical energy into electricity came to my mind around August 2005, when we were measuring the electromechanical coupled properties of the wires. Using an atomic force microscope (AFM), we observed some voltage output peaks, but we were not sure what they were. We did systematic work through November of that year and learned that the voltage was from the piezoelectric effect of the zinc oxide; our results excluded the contribution from friction, contact or

[THE BASICS]

MECHANICAL ENERGY TO ELECTRICITY

A nanogenerator (*below left*) consists of an array of vertical zinc oxide nanowires, hexagonal crystals with both piezoelectric and semiconducting properties. A rectangular electrode with a ridged underside sits atop the nanowires and moves side to side in response to external

forces such as vibration, the human pulse or acoustic waves. In this example, the generator's output is stored in a capacitor and periodically sent to a sensor, which could be measuring blood glucose or pressure. A tiny radio-frequency transmitter reports the results.



GEORGE RETSECK

other confounding artifacts. The next step was determining what the process was for the charge output from a single nanowire. After studying a book on semiconductor devices, I proposed the working mechanism of what would become the nanogenerator.

Zinc oxide has the rare attribute of possessing both piezoelectric and semiconducting properties, which we put to use in creating and accumulating piezoelectric charges in the nanowires. We have shown that when the conductive tip of an AFM bends a straight, vertical nanowire, a strain field is established, with the stretched surface showing positive strain and the compressed surface showing negative strain. As the tip scans over the top of the zinc oxide nanowires, we observe many peaks in the corresponding voltage output image for each contact position [see box on page 84]. The piezoelectric effect creates an electric field inside the nanowire's volume, with the stretched and compressed sides of the wire showing positive and negative voltages.

The idea came first, but we needed experimental support. Just before Christmas 2005, I designed an experiment to visualize directly the voltage output of a large wire under optical and AFM microscopy. My student and I did the experiments, and one evening in late December, we were rewarded with several videos that directly proved my model. The next day I worked with Jinhui Song in my office to edit the movie. Then we sent the paper to *Science* for publication.

To be useful in practical applications, our nanogenerator needs to contain an array of nanowires, all of them continuously generating electricity that can be collected and delivered to a device. And the energy to be converted into electricity has to come in the form of a wave or vibration from the environment so the nanogenerator can operate independently and wirelessly. We have developed a novel design that addresses these requirements.

The next challenge was to increase the power of the nanogenerator. Three objectives have to be achieved: eliminate the use of the AFM, make many nanowires generate electricity simultaneously and continuously, and excite the nanowires in an indirect wave, such as an ultrasonic wave. I came out with a new design using a ridged electrode to replace the AFM tips and presented the idea to my postdoctoral assistant, Xudong Wang. It took him about four months of experiments before compiling the first group of data. The signal was rather small. From May to October 2006 we focused on the

optimum packaging of the nanogenerator to enhance its output. By the end of the year we realized that the nanogenerator could at last be reported to the scientific community.

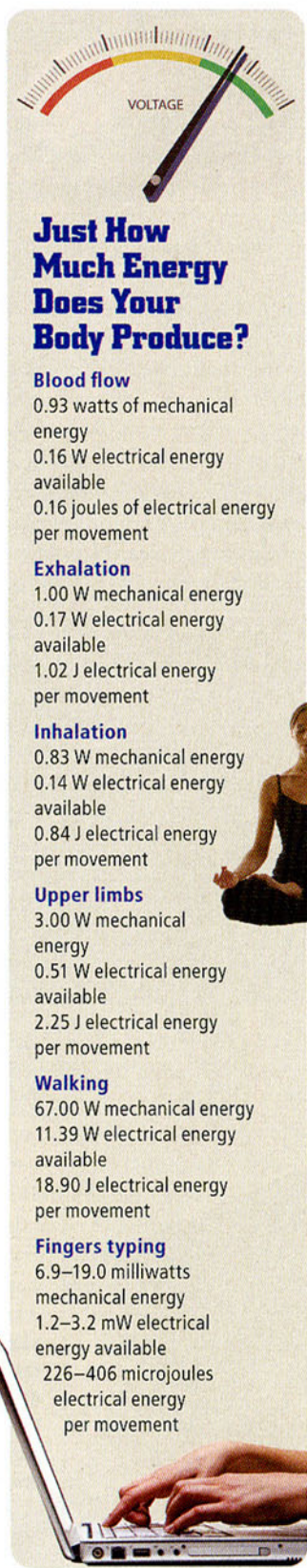
Our experimental setup provided the first demonstration of continuous direct current produced by a piezoelectric nanogenerator. It consists of an array of parallel zinc oxide nanowires and a platinum-coated silicon electrode with a ridged surface in place of the microscope's tip. Coating the electrode with platinum both enhances its conductivity and causes it to act like a diode that allows current to flow in only one direction, from metal to semiconductor. The electrode is placed above the nanowire array at a controlled distance and can be moved laterally so that it bends the nanowires from side to side. Thanks to its surface ridges, the electrode acts like an array of aligned microscope tips [see box on preceding page].

Flexible Future

Since January 2007 we have been fully involved in improving our nanogenerator. The ceramic or semiconductor substrates that we initially used for growing zinc oxide nanowires are hard and brittle, for instance, making them unsuitable for applications that require a foldable or flexible power source, such as biosensors implanted in muscles or joints, or power generators built into shoes.

Here is where conductive polymers can provide a substrate that is likely to be biocompatible. In experiments we discovered that many available flexible plastic substrates are suitable for growing the zinc oxide nanowire arrays, which ultimately could find applications in portable and flexible electronics. Because of the flexibility of the substrate, the nanowire surface profile was wavy, causing some missed contacts. We believe that providing suitable bonding strength between the nanowires and substrate as well as optimizing the wire spacing will be important in increasing discharge efficiency.

Although our approach has demonstrated the principle of the nanogenerator, we must drastically improve its performance to make it practical. All the nanowires must generate electricity simultaneously and continuously, and all the electricity must be effectively collected and distributed. A large-scale method for growing zinc oxide nanowires can be cost-effective because it does not require expensive high-temperature manufacturing processes. Hurdles that lie ahead



Just How Much Energy Does Your Body Produce?

Blood flow
 0.93 watts of mechanical energy
 0.16 W electrical energy available
 0.16 joules of electrical energy per movement

Exhalation
 1.00 W mechanical energy
 0.17 W electrical energy available
 1.02 J electrical energy per movement

Inhalation
 0.83 W mechanical energy
 0.14 W electrical energy available
 0.84 J electrical energy per movement

Upper limbs
 3.00 W mechanical energy
 0.51 W electrical energy available
 2.25 J electrical energy per movement

Walking
 67.00 W mechanical energy
 11.39 W electrical energy available
 18.90 J electrical energy per movement

Fingers typing
 6.9–19.0 milliwatts mechanical energy
 1.2–3.2 mW electrical energy available
 226–406 microjoules electrical energy per movement

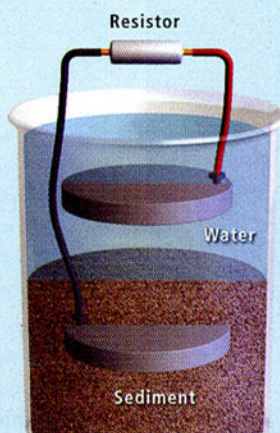
Ambient-Energy Harvesters

Nanogenerators that use vibration-driven piezoelectrics show promise, but other ways to siphon energy from the environment also exist

The most effective energy-harvesting processes are in nature, such as in microorganisms that must perform this task to survive. Derek R. Lovley of the University of Massachusetts Amherst and his colleagues, for instance, have reported that a marine organism, *Desulfuromonas acetoxidans*, can transfer electrons to a graphite electrode from acetate produced in sea sediments by other organisms. The result is an electric current that flows through water to another electrode. Such "sediment batteries" might be used for bioremediation of toxic wastes, for example. Similarly, the catalytic action of microorganisms can produce electrical output from different carbohydrates and substrates.

In 2004 a group of researchers led by A. K. Shukla of the Central Electrochemical Research Institute in India demonstrated biological fuel cells that use organic substances and metabolic processes to generate current. It is possible to tap into the body's own resources, including the metabolic properties of our cells, to generate enough energy to power an array of medical devices, including drug delivery systems, cardiac pacemakers and diagnostic devices. The drawback of microbial fuel cells is that their size is rather large and their power output may not be adequate for nonbiological applications.

Another option, a thermoelectric generator, relies on the Seebeck ef-

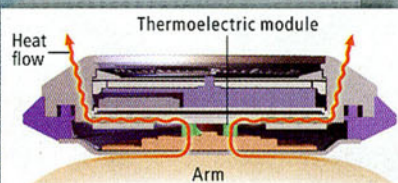


SEDIMENT battery is powered by marine organisms.

fect, wherein an electric potential exists at the junction of two dissimilar metals that are at different temperatures. The voltage produced is proportional to the temperature difference between the two ends; thermocouples based on this principle are often used to measure temperature. When a temperature difference is applied, charge carriers in the material diffuse from the hot side to the cold side. Mobile charge carriers migrating to the cold side leave behind their oppositely charged and immobile nuclei at the hot side, giving rise to a thermoelectric voltage.

Thermoelectrics is an exciting field, but the generators are fairly large because of the need to maintain an appreciable temperature difference between the two ends of the device. Consequently, thermoelectric generators may have limited applications as power sources that can be integrated into nanosystems. Yet they have already found some commercial applications, such as the Seiko Thermic wristwatch, introduced in 1998, which used thermoelectric modules to generate sufficient microwatts to run its mechanical workings from the small gradient between the wearer's body heat and the ambient temperature.

—Z.L.W.



THERMOELECTRIC generator exploits temperature differences.

in our research include learning how to grow perfectly uniform arrays of nanowires that all produce electricity and how to extend their working life. The lifetime of the current nanogenerator is about 50 hours. The main reason for the device's failure is likely the packaging technology for assembling the top electrode and the nanowire arrays. If the electrode presses on the nanowires too firmly, for example, no current will be generated. We are working hard to improve the packaging.

The process used to produce the arrays involves evaporating a thin layer of gold onto the substrate, where it acts as a catalyst for nanowire growth. The zinc oxide crystals look something like a forest without branches. To improve the adhesion of the nanowires with the substrate, we have added a thin layer of polymer onto the substrate after growth so that the roots of the nanowires are partially embedded. We have achieved electrical output of about 10 millivolts and 800 nanoamperes from a nano-

generator that is about six square millimeters in size. We have also shown that nanogenerators can be arranged in series to improve the output voltage and in parallel to improve the output current, as is commonly done with power sources such as batteries or fuel cells. But to produce higher voltages, we need to make nanowires with identical height and diameter.

Nanogenerators may never power our homes or even our flashlights; the amount of power available from them will be quite small. But nanowire arrays can be ideal generators for devices that need to work only intermittently, such as sensors that collect and transmit data for one second of every minute. In the years to come, nanogenerators will be used to harvest and recycle the energy wasted in our daily life, such as that created by pressure changes in a car tire, a moving vehicle's mechanical vibration or even the fluttering surface of a camper's tent. Consider how many small energy resources are all around us.

➔ MORE TO EXPLORE

Direct-Current Nanogenerator Driven by Ultrasonic Waves. Xudong Wang, Jinhui Song, Jin Liu and Zhong Lin Wang in *Science*, Vol. 316, pages 102–105; April 6, 2007.

Nanowire Piezoelectric Nanogenerators on Plastic Substrates as Flexible Power Sources for Nanodevices. Pu Xian Gao, Jinhui Song, Jin Liu and Zhong Lin Wang in *Advanced Materials*, Vol. 19, pages 67–72; 2007.

Zhong Lin Wang's Web site is available at www.nanoscience.gatech.edu/zlwang