



The road less traveled to nanowire sensors

One researcher fabricated his nanowires in an unusual way, and that has made all the difference.

When Reg Penner began to think about nanowires, the University of California (UC), Irvine, researcher asked himself what any good electrochemist would: What can I detect with them?

The fundamentals of sensing with carbon nanotubes were reported in *Science* in 2000 by two groups that described changes in the conductivity of nanowires upon exposure to various gases (2000, 287, 622–625; 1801–1804). But relatively few papers about nanowire sensors were published subsequently (e.g., *Science* 2001, 293, 1289–1292; 2227–2231), indicating that some serious obstacles lay in the path to practical implementation.

“I think one of the [factors] that’s neglected in this whole nanosensing business, whether it’s particles or wires or films, is the importance of the stability of the material,” says Penner. Because nanowires are made with such small amounts of material, they are “incredibly fragile” mechanically and chemically, he explains. “I really do think that progress has been impeded by this stability problem.”

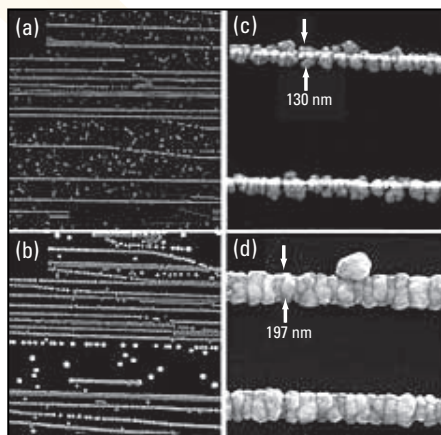
Penner suspected that the choice of materials for nanowires—typically, semiconductors—could be part of the problem, so he decided to work with noble metals. “[I]n a lot of ways, they would be superior to using semiconductors,” he says. Thin metal films will register increases in resistance if analytes adsorb on the surface. Although the change is small (1–5%), the S/N is good, he explains. And gold, silver, and platinum resist oxidation in aqueous solutions and over a broad range of pH.

So, Penner decided to make nanowires from silver. The “only” issue his group had to tackle was fabrication.

Why noble metals matter

The researchers found noble-metal nanowires quite difficult to grow, so they developed an electrochemical meth-

od for nucleating wires on the edges of a graphite substrate, which is cut like a flight of steps with long treads (*Nano Lett.* 2004, 4, 665–670). The researchers oxidized the substrate gently and applied a negative nucleation pulse (–1 V) for 100 ms. Silver nuclei, 5–20 nm in diameter, formed on the graphite edges,



Scanning electron micrographs of Ag wires grown for (a, c) 30 s or (b, d) 1500 s. (Adapted from *Anal. Chem.* 2005, 77, 5205–5214.)

and the researchers let them grow for ~100 s to ~1 h until they coalesced.

The mesowires—at 150–950 nm in diameter, they were larger than true nanowires—looked like densely packed beads on a string. The researchers exposed them to ammonia and other amine vapors and measured the resulting resistance changes. Gold, copper, platinum, and silver wires showed resistance increases as high as several hundred percent. But for the silver wires, the change was reversible: When the ammonia was removed, the resistance dropped to its original value within seconds (*Anal. Chem.* 2005, 77, 5205–5214). Although the mesowires looked identical to one another, some registered increases of <1%, whereas others had changes of ~10,000%.

“We pretty quickly understood after doing some literature research that the resistance effects that we were seeing were much larger than we should expect,” Penner explains. In the hundreds of papers published about the chemisorption of molecules on very thin films, he says, “the resistance change that people see with very thin films [is] always <5% or 6%. We didn’t see a single paper where the effect was >6%.”

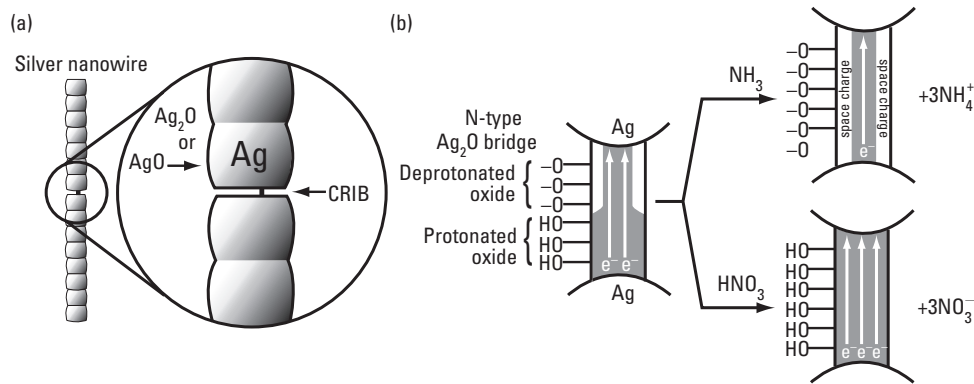
It’s all in the oxide

One model that might have accounted for Penner’s surprising data was published by Nongjian Tao at Arizona State University (*J. Am. Chem. Soc.* 2001, 123, 4585–4590). Tao etched gold wires to make them very thin, and right before the wires broke, he measured a stepwise decrease in conductivity; this indicated that Tao had prepared a quantum point contact. When he exposed these quantum point contacts to adsorbing molecules, such as amines, he observed large resistance increases.

Penner assumed that his group was seeing a similar effect. “The constrictions in our systems, then, would be at grain boundaries along the axis of the wires,” he says. “That’s where we hypothesized that this ‘Tao effect’ was happening.”

“There were so many things about the Tao mechanism that made sense,” says Penner. “I really wanted it to work that way. And I thought it was really neat that these quantum point contacts could be embedded in these nanowires.” He hoped that he had found a way to fabricate the quantum point contacts in an easy-to-use, connectable form.

Penner’s students Erich Walter and Ben Murray spent ~6 months trying to explain their results in that context, but the data just didn’t fit. Later, the students did some experiments “that really



Schematic diagrams of (a) a CRIB and (b) the mechanism by which resistance in CRIBs is modulated by bases such as NH₃ and acids such as HNO₃. (Adapted from *Anal. Chem.* **2005**, *77*, 5205–5214.)

forced us to think about the mechanism” in a new way, says Penner.

Walter and Murray measured the resistance as a function of temperature for various sensors with different responses to ammonia. For all of the mesowires, the temperature dependence of the resistance was weaker than expected for silver metal. In fact, on average, the stronger the response to ammonia, the larger the deviation. Some especially strong sensors even showed an inverted temperature dependence—the resistance decreased with increasing temperature.

“That didn’t make sense in terms of the Tao model at all,” Penner says. “In [that] model, you’ve got an all-metallic system, and you really expect to see a metal-like temperature dependence no matter what.”

Because of the mismatch with the Tao model, Penner’s group began to develop their own hypothesis. The literature on sensors indicates that metal-oxide-based surfaces can detect acids and bases. So they speculated that silver oxide bridges were forming between the grains in their bead-like nanowires and acting as n-type semiconductors. These constrictions gated the conduction, thereby imparting sensitivity to the vapors of either acids or bases.

The researchers examined the nanowires with conductive-tip atomic force microscopy and noted that individual wires could have hot (responsive to ammonia) and cold (nonresponsive) segments. The responsive segments had much higher resistances, but only a

small minority (~10%) of the segments exhibited the effect. These observations were consistent with their hypothesis.

Nevertheless, for this idea to have any credibility, the researchers would have to locate the metal oxide in their wires. They collaborated with John Hemminger at UC-Irvine, who used X-ray photoelectron spectroscopy (XPS) to conduct the search. It was fruitless.

“Our collaborators couldn’t detect any oxide on these wires at all,” says Penner. “That was very frustrating to us.”

CRIBs are christened

To resolve the matter, the researchers oxidized the wires by electrodepositing Ag₂O on the surfaces for ~10 s. When examined by XPS, those wires did show evidence of Ag₂O. “When we measured the ammonia sensitivity of those wires, they were always strong sensors,” adds Penner. “The weakest sensor we ever saw” exhibited a 25% change. Moreover, the researchers could transform weak sensors into strong sensors with this oxidation step.

Later, the researchers made solid silver oxide wires. “That should have been the first thing we did,” concedes Penner, but it “was very hard for us to do.” These wires were very sensitive to ammonia—identical to what the researchers saw for the earlier wires (*Chem. Mater.* **2005**, *17*, 6611–6618). Encouraged by these findings, they gave the oxide bridges between two silver grains a name, chemically responsive interparticle boundaries (CRIBs).

To confirm their model, they performed some photoconductivity experiments. They expected that sensors that responded well to amine vapors would exhibit photoconductivity, whereas poor sensors would not. According to the Tao model, the junctions wouldn’t show any photoconductivity response.

Unfortunately, the experiments did not provide an authoritative answer. The researchers did observe photoconductivity in sensors that responded well to amine vapors, and the onset of the effect occurred at an energy that coincided with Ag₂O. This result was

enough to rule out the Tao model. But it wasn’t enough to confirm their own model, because they observed the effect in only ~5% of good sensors; they had expected to see it in 100%.

Penner never published these results. He suspects that in many of the wires, the bridges are recessed so deeply within the boundaries that light can’t reach them; that’s why some of the good sensors didn’t pass the photoconductivity test. But the wires are so small that it’s hard to test this idea.

Now, his group is working on sensors for practical use. To impart selectivity, they are trying to attach molecular recognition moieties directly to the oxide by using phosphonates and carboxylates to form covalent bonds. And because gold is chemically robust in environments where one might want to use a sensor, the team wants to make gold nanowires with CRIBs. They also want to adapt work that they have done with Gregory Weiss at UC-Irvine on “virus electrodes”. These are gold electrodes that bear a self-assembled monolayer of M13 phage, modified to bind prostate-specific membrane antigen (*Anal. Chem.* **2006**, doi 10.1021/ac052287u). Now Penner wants to attach the phage to gold wires.

Penner isn’t sure how much of what he learned about CRIBs holds true for traditional nanowires, because some of it seems to be peculiar to the fabrication method he chose. What a critical—and fortunate—choice that turned out to be. ■

—Elizabeth Zubritsky