

Nano Focus

Gold nanoparticles tailored to visualize fingerprints in reverse

When forensic scientists attempt to visualize latent fingerprints, they typically rely on reagents that respond to amino acids or sebaceous materials. This type of visualization makes fingerprint ridges more apparent, but the quality of the print is highly reliant on the amount of residue left behind. As Sanaa Shenawi, Nimer Jaber, Joseph Almog, and Daniel Mandler from the Hebrew University of Jerusalem have reported in the May issue of *Chemical Communications* (DOI: 10.1039/c3cc41610k; p. 3688), fingerprints on paper can now be visualized with a chemical method that enhances the areas of the paper

that are not covered by sebaceous matter. With this technique, the sebaceous material serves as a mask that protects the paper from the chemical reaction, and the prints appear as a “negative” or “reversed” image. According to Almog, “Despite the plethora of quite sophisticated fingerprint reagents that currently exist, there is still a need for more sensitive ones, since in criminal investigations, a considerable portion of the latent prints still escape detection.”

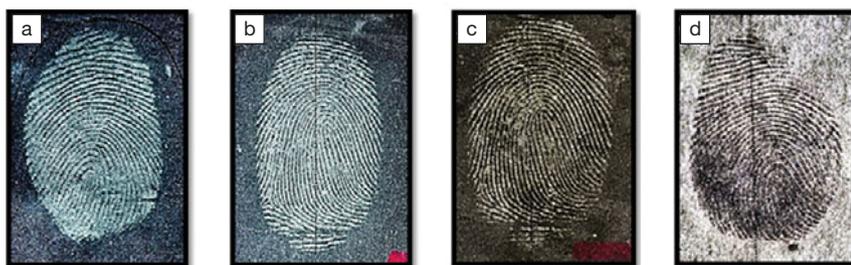
Gold nanoparticles were capped with various mercaptocarboxylic acids. This class of acids contains thiol groups, which can readily bind to gold, and carboxylic groups, which can form hydrogen bonds with cellulose. After preparing strips of paper with fingerprint marks, the strips were placed into a nanoparticle solution

for a few minutes. Afterwards, a silver developer was used to make the fingerprints apparent. Developing is based on localized electroless silver deposition catalyzed by the gold nanoparticles. Thus, silver deposits almost exclusively on the areas where the gold nanoparticles were previously attached. The location of this step was found to depend on the actual ligand used with the gold.

When short-chain ligands were used, strong hydrogen bonds formed between the ligands and the cellulose in the paper. As a result, the paper was coated with gold, except the sebaceous areas. After applying the silver, a reversed fingerprint appeared, because the silver coated everything except for the sebaceous areas. The best ligand for reverse imaging proved to be 3-mercaptopropionic acid. When it was used, fingerprints as old as 14 months were developed with high contrast. However, when longer chain ligands were used on the gold, the nanoparticles developed a stronger affinity toward the sebaceous ridges. Thus, after treatment with silver, the fingerprint ridges were stained instead of the cellulose areas.

The researchers said that this new “reversed” method to developing fingerprints is a step forward in the science, since it is less reliant on the content of the sebaceous materials than other current visualization methods.

Anthony S. Stender



The images of fingerprints were developed by treatment with gold nanoparticles capped with different mercaptocarboxylic acids followed by silver deposition: (a) 3-mercaptopropionic acid on fresh print; (b) 3-mercaptopropionic acid on 14-month-old print; (c) 4-mercaptobenzoic acid on fresh print; and (d) 11-mercaptoundecanoic acid on fresh print produces “positive” print, not a “reversed” print, unlike the prior three images. Reproduced with permission from *Chem. Commun.* DOI: 10.1039/c3cc41610k; p. 3688. © 2013 The Royal Society of Chemistry.

Bio Focus

Is zinc the perfect material for bioabsorbable stents?

To help with narrowed or obstructed arteries, surgeons typically perform balloon angioplasty, a procedure that first widens the blood vessels with a balloon and then keeps them propped open with a wire mesh called a stent. The metal stents permanently stay in the body, potentially causing issues such as chronic inflammation and local clotting. Scientists have now discovered that stents made from bioabsorbable zinc could be exactly what clinicians and patients need—

they could give arteries enough time to heal but not linger in the body long enough to cause additional problems.

“We found that the degradation rate of zinc is perfect,” said Jaroslav Drellich, a materials researcher at the Michigan Technological University and co-author of the new study, published in the May 14 issue of *Advanced Materials* (DOI: 10.1002/adma.201300226; p. 2577).

In the last decade, scientists have looked into the efficacy of bioabsorbable stents, focusing on iron- and magnesium-based stents. Iron stents are not ideal because the material produces a large volume of potentially hazardous

iron oxide, which does not degrade easily in the human body. And magnesium is innocuous but dissolves in the body much too quickly. The research team decided to start with a different metal as a base material. They chose zinc because previous research has shown that zinc can help slow down the biodegradation process when added to other materials.

To test the biodegradation properties of metallic zinc, graduate student Patrick Bowen crafted 15-mm-long zinc wires. The wires, which were less than half a millimeter in diameter, did not comprise a full stent—they represented a supportive portion of the stent called a

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strut, Drelich said. Collaborator Jeremy Goldman, a biomedical engineer, placed these tiny wires into the abdominal aorta of rats, and then removed and examined the wires' corrosion after 1.5, 3, 4.5, and 6 months.

For the first three months, the researchers found that the zinc wires degraded in the rats at a rate that they calculated as just below 20 μm a year, the ideal corrosion rate. At four months, the pure zinc still retained about 70% of its cross-sectional area, and then its degradation rate accelerated rapidly, ensuring that it would not stay in the body for too long. Moreover, the team saw that more

healthy arterial tissue stuck to the wires the longer the wires remained in the body, suggesting that the zinc was not damaging the arterial walls. And because zinc is known to fight arterial plaque, a zinc-based stent could further help patients suffering from ischemic problems.

Carlo Di Mario, a clinical cardiologist at Imperial College London who was not involved in the research, said that the work is interesting and it appears that zinc-based stents would last longer in the body than magnesium-based stents. However, he said that the low tensile strength of zinc is an issue: The wires work perfectly in rats, but the material

is not strong enough to hold open human arteries. Using zinc alloys is necessary, but "the avenue to alloys seems a bit too long for a clinician to be interested at this stage," Di Mario said.

However, Drelich said they are already testing promising new zinc alloys to fix the strength issue—the invented alloys meet all of the benchmarks necessary for a bioabsorbable stent material candidate. The team is now continuing *in vivo* testing of new alloys and expects to complete prototype mini-stents this year. Within a few years, they should be ready to move on to clinical trials, he said.

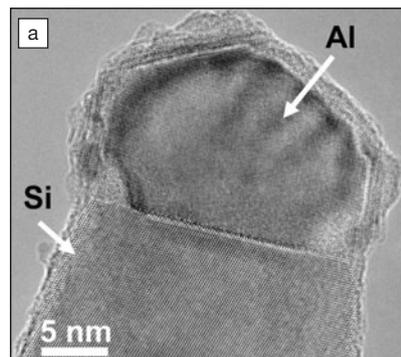
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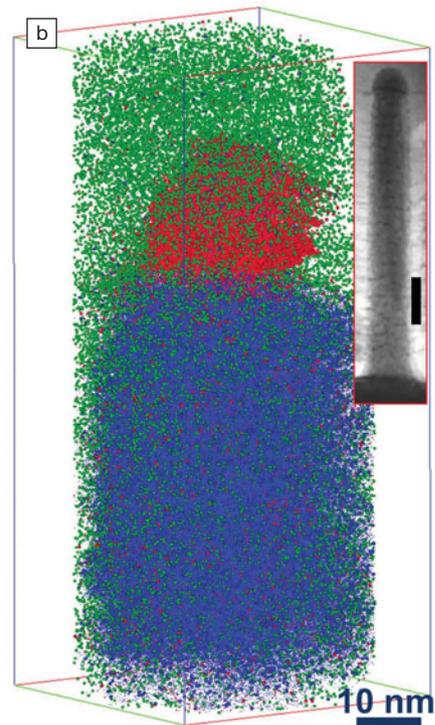
Al catalyst yields massive doping of Si nanowires

Semiconductor nanowires represent versatile nanoscale building blocks, finding applications as new transistors and circuits for next-generation electronics, as well as in photonics, solar cells, biosensing, and neuro-engineering technology. Silicon nanowires have attracted particular interest, where their properties are controlled by doping with foreign ions. It has recently been demonstrated that aluminum provides an effective growth catalyst for silicon nanowires, where the aluminum also provides an effective *p*-type dopant, being homogeneously distributed throughout the silicon.

As reported in the April 4 issue of *Nature* (DOI: 10.1038/nature11999; p. 78), an international team of researchers from École Polytechnique de Montréal in Canada, Max Planck Institute of Microstructure Physics in Germany, and Northwestern University in Illinois have now gained an atomic-level understanding of this process. Silicon nanowires were grown by heating a silicon substrate supporting aluminum islands to a temperature where only the aluminum melts, and not the silicon. The substrate was then exposed to a vapor-phase silane reactant. Part (a) in the figure shows how the surface of an aluminum drop adsorbs silicon



(a) The high-resolution transmission electron microscope image shows the interface between aluminum and silicon (© Nature/MPI of Microstructure Physics). (b) Atom probe tomography reveals the atomic structure of the material: red shows the representative positions of the aluminum atoms and blue those of the silicon atoms. An analysis of the data shows the very high concentration of aluminum in the silicon and its uniform distribution. For experimental reasons, the nanowire was coated with a protective layer of nickel (green) for the analysis. Inset: size marker is 40 nm. (© Nature/Northwestern University, Illinois)



from the silane, which then migrates to the bottom of the drop where it deposits in layers. Significantly more aluminum is thus embedded in the silicon wire than was to be expected theoretically.

"The silicon here takes up as much as 10,000 times more aluminum than the laws of thermodynamics allow," said Eckhard Pippel, one of the participating researchers from the Max Planck Institute of Microstructure Physics.

Theoretically, fewer than one in a million atoms should be replaced by aluminum in a silicon crystal. However, the aluminum content of the silicon wires is actually around 4%. Co-researcher David Seidman, the Walter P. Murphy Professor of Materials Science and Engineering at Northwestern, and Dieter Isheim, Research Assistant Professor, said, "We could see that aluminum triggers a self-doping process that results