Green meets nano: Scientists create multifunctional nanotubes using nontoxic materials

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A doctoral student in materials science at Technische Universitat Darmstadt is making multifunctional nanotubes of gold—with the help of vitamin C and other harmless substances.

Coffee, apple juice, and vitamin C: things that people ingest every day are experimental material for chemist Eva-Maria Felix. The doctoral student in the research group of Professor Wolfgang Ensinger in the Department of Material Analysis is working on making nanotubes of gold. She precipitates the precious metal from an aqueous solution onto a pretreated film with many tiny channels. The metal on the walls of the channels adopts the shape of nanotubes; the film is then dissolved. The technique itself is not new, but Felix has modified it: "The chemicals that are usually used for this were just too toxic for me." She preferred not to use cyanide, formaldehyde, arsenic and heavy metal salts. She was inspired by a journal article by researchers who achieved silver precipitation using coffee.

Felix also used coffee in her first experiments. She then tested apple juice, followed by vitamin C. This seemed to be the best suited to her because "you never know what's in coffee and apple juice." On the other hand, Vitamin C - or ascorbic acid - is available in pure form from chemical stores - a requirement for reproducible studies. But what does the vitamin have to do with the precipitation of gold? In the human body, vitamin C makes free radicals harmless by transferring electrons to them. "Gold precipitation functions according to the same principle. The only difference is that the vitamin does not take on radicals, but rather gold ions", explains Falk Münch, a postdoctoral researcher and supervisor of Felix' PhD thesis. The gold ions that are dissolved in the precipitation bath are transformed into metallic gold after absorbing electrons.

Additional, harmless chemicals are required for the process. But the procedure is green not only because of the non-toxic substances, but also because it takes place at room temperature and without an external power supply, thus saving energy. Furthermore, as opposed to other methods, no expensive devices are required. The film with the nanochannels is merely placed in the precipitation bath. "It's really unbelievable that aqueous solutions and simple basic chemicals can produce such precise nanostructures" says Münch.

"Green meets Nano" is a motto of the researchers at the TU. The only thing that is not green in the procedure is the film that is used as the template, notes Ensinger. Although tests with bio-based plastics are already on the agenda, the films still consist of polycarbonate also made or of polyethylene terephthalate (PET).

In order to create the miniature plastic channels that define the shape, a round film is vertically bombarded with an ion beam. Each ion leaves a straight track in the film which then becomes a small hole, or, when seen through the microscope: a channel that is then etched. Its diameter can be set precisely - down to far less than 100 nanometers. The gold nanotubes are thus several hundred times finer than a human hair. Their wall thickness depends both on the duration of precipitation and on the gold concentration of the original solution. After the film is dissolved, the result is - depending on the experimental conditions - a collection of individual nanotubes or an array of hundreds of thousands of interconnected tubes.

The crux of the technique: an ion accelerator is needed to generate an ion beam. The TU scientists found the ideal partner for their research in the GSI Helmholtz Center for Heavy Ion Research at the outskirts of Darmstadt; but the GSI's large-scale accelerator was not suitable for subsequent commercial use for financial reasons. The TU scientists are already looking for alternatives. For example, a company in the USA produces similarly perforated films with smaller accelerators. "The films are not as well-defined as ours are, but they are also suitable", says Münch. Furthermore, they are inexpensive: a film roughly the size of a sheet of paper costs only a few euros. Ensinger says that the price of gold is not a factor because the amounts that are required are small: "With 1 gram of gold, we could make a nanotube for literally every person on earth." Although a single tube is not useful for anyone, not much material is needed for microsensors, miniature through-flow reactors, or other potential applications.

Ensinger's team has already successfully tested one use of the gold nanotubes: they are suitable for building sensors to measure hydrogen peroxide. This chemical damages nerve cells and apparently plays a role in neurodegenerative diseases such as Alzheimer's and Parkinson's. A microsensor that can measure hydrogen peroxide in the human body would thus be practical both in medical research as well as for diagnosis. The conversion of hydrogen peroxide to water, catalyzed by the gold releases electrons generates an easily measurable electric current. The gold nanotubes conduct electricity especially well due to their one-dimensional structure. In addition, they are relatively long and are thus more durable than normal nanoparticles.

"Nano meets Life" is the second motto of the TU Materials Science researchers. For example, they are thinking about also using the nanotubes to measure blood sugar. "A subcutaneous sensor could save diabetes patients from having to constantly prick their fingers" thinks Ensinger. The green method of production also has advantages here because the components of such implants should be produced with as few toxic chemicals as possible. "This completes the circle", says the TU professor, combining the two mottos: "Green meets Nano meets Life".

More information: Eva-Maria Felix, Falk Münch and Wolfgang Ensinger published their green method for generating gold nanotubes and their suitability as hydrogen peroxide sensors in the specialist journal RSC Advances of the British Royal Society of Chemistry, *RSC Advances* 4, 24504-24510, 2014, [DOI: 10.1039/c4ra03377a](DOI: 10.1039/c4ra03377a)

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