Researchers make carbon nanotubes without metal catalyst

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(PhysOrg.com) -- Carbon nanotubes — tiny, rolled-up tubes of graphite — promise to add speed to electronic circuits and strength to materials like carbon composites, used in airplanes and racecars. A major problem, however, is that the metals used to grow nanotubes react unfavorably with materials found in circuits and composites. But now, researchers at MIT have for the first time shown that nanotubes can grow without a metal catalyst. The researchers demonstrate that zirconium oxide, the same compound found in cubic zirconia “fake diamonds,” can also grow nanotubes, but without the unwanted side effects of metal.

The implications of ditching metals in the production of carbon nanotubes are great. Historically, nanotubes have been grown with elements such as iron, gold and cobalt. But these can be toxic and cause problems in clean room environments. Moreover, the use of metals in nanotube synthesis makes it difficult to view the formation process using infrared spectroscopy, a challenge that has kept researchers in the dark about some of the aspects of nanotube growth.

“I think this fundamentally changes the discussion about how we understand carbon nanotubes synthesis,” says Brian Wardle, professor of aeronautics and astronautics who led the study, published Aug. 10 in the online version of the Journal of the American Chemical Society.

Wardle adds that some researchers might find the result controversial since no one has ever proven that anything other than a metal can grow a nanotube. “People report new metals [as catalysts] every so often,” he says. “But now we have a whole new class of catalyst and new mechanism to understand and debate.”

The conventional model for nanotube growth goes like this: A substrate is sprinkled with nanoparticle seeds made of a certain metal, of the same diameter of the desired nanotubes. The substrate and nanoparticles are heated to 600 to 900 degrees Celsius, and then a carbon-containing gas such as methane or alcohol is added. At the high temperatures, molecules break apart and reassemble. Some of these carbon-containing molecules find their way to the surface of a nanoparticle where they dissolve and then precipitate out, in nanotube form.

The researchers found that if they just used zirconium oxide nanoparticles on the substrate, they could coax carbon into nanotubes as well. Importantly, the mechanism for growth seems to be completely different from that of metal nanoparticle-grown tubes. Instead of dissolving into the nanoparticle and precipating out, zirconia-grown nanotubes appear to assemble directly on the surface.

In collaboration with Professor Stephan Hofmann at the University of Cambridge in England, the MIT researchers took images of the oxide-based nanotubes using X-ray photoelectron spectroscopy during growth. This allowed them to see that when nanotubes formed, zirconium oxide persisted, and didn’t form into a metal, bolstering their conclusions.

One of the most exciting implications of the finding is that it means that carbon fiber and composites, used to make different types of crafts, could be strengthened by nanotubes. “Composites are durable, but fail under certain loading conditions, like when plywood flakes and splinters apart,” says Stephen Steiner, an MIT graduate student and the study’s first author. “But what if you could reinforce composites at the microlevel with nanotubes the way that rebar reinforces concrete in a building or a bridge? That's what we're trying to do to improve the mechanical properties and resistance to fracturing of carbon composites."

Steiner says the reason that planes like Airbus' A380 and Boeing's new 787 are made of only 40 percent composites and not 90 percent is because composites aren't strong enough for all parts of the craft. But if they were bolstered by nanotubes, then the planes could be made of more composites, which would make them lighter, and less expensive to fly because they wouldn't need as much fuel.

The findings are already impressing researchers in industry. "This innovation has far-reaching implications for commercial productions of carbon nanotubes," says David Lashmore, CTO of Nanocomp Technologies Inc., a company in Concord, N.H., that was not involved in the research. "It for the first time allows the use of a ceramic catalyst instead of a magnetic transition metal, some of which are carcinogenic."

Wardle suspects that more oxide-based catalysts will be found in the coming years. He and his team will focus on trying to understand the fundamental mechanisms of this type of nanotube growth and help to contribute more types of catalysts to the nanotube-growing arsenal. While the researchers don't have a timeline, they suspect that it would be easy to commercialize the process as it's simple, adaptable and, in many ways, more flexible than growth with metal catalysts.

More information: JACS paper available online: pubs.acs.org/doi/full/10.1021/ja902913r

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