Researchers learn to control the dimensions of metal oxide nanotubes

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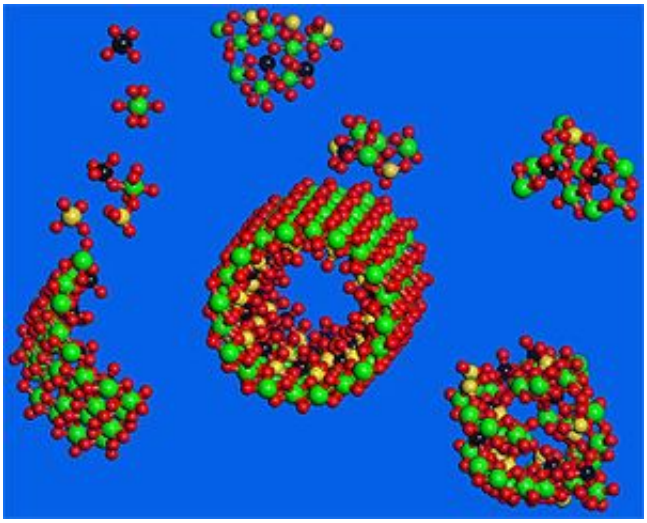

Computer-generated graphic shows a single-walled metal oxide nanotube assembling itself from small molecules and amorphous nanoparticles dissolved in water. Image courtesy of Suchitra Konduri

Moving beyond carbon nanotubes, researchers are developing insights into a remarkable class of tubular nanomaterials that can be produced in water with a high degree of control over their diameter and length. Based on metal oxides in combination with silicon and germanium, such single-walled inorganic nanotubes could be useful in a range of nanotechnology applications that require precise control over nanotube dimensions.

At the Georgia Institute of Technology, researchers are studying the

formation of these metal oxide nanotubes to understand the key factors that drive the emergence of nanotubes with specific diameters and lengths from a “soup” of precursor chemicals dissolved in water. Their goal is to develop general guidelines for controlling nanotube diameter with sub-nanometer precision and nanotube length with precision of a few nanometers.

So far, the researchers have obtained encouraging results with a model system that produces aluminosilicogermanate (AlSiGeO) nanotubes. The research, which will be presented August 23rd at the 234th National Meeting of the American Chemical Society, could open the door for developing a more general set of chemical “rules” for dimensional control of nanotubes that could lead to a range of new applications for inorganic nanotubes and other nanometer-scale materials. The research has been sponsored by the American Chemical Society Petroleum Research Fund.

“We have shown that there is a clearly quantifiable molecular-level structural and thermodynamic basis for tuning the diameter of nanotubes,” said Sankar Nair, an assistant professor in Georgia Tech’s School of Chemical and Biomolecular Engineering. “We’re interested in developing the science of these materials to the point that we can manipulate their curvature, length and internal structure in a sophisticated way through inexpensive water-based chemistry under mild conditions.”

Using chemical reactions carried out in water at less than 100 degrees Celsius, Nair’s research team – which included graduate students Suchitra Konduri and Sanjoy Mukherjee – varied the germanium and silicon content during the nanotube synthesis and then quantitatively characterized the resulting nanotubes with a variety of analytical techniques to show a clear link between the nanotube composition and diameter.

Simultaneously, the group's molecular dynamics calculations showed a strong correlation between the composition, diameter and internal energy of the material.

"There appear to be energy minima that favor or stabilize certain nanotube diameters because they have the lowest energy, and those stable diameters change with the composition of the material," said Nair. "This shows that the nanotube dimensions are not just a fortuitous coincidence of the many synthesis parameters, but that there is an underlying thermodynamic basis arising from the subtle balance of interatomic forces within the material."

Specifically, the molecular dynamics simulations – which are corroborated by the experiments – show that the variation of germanium and silicon content causes sheets of aluminum hydroxide to form nanotubes with diameters ranging from 1.5 to 4.8 nanometers and lengths of less than 100 nanometers. If that turns out to be a general principle applicable to other metal oxides, it could be used to dramatically expand the catalog of nanotube structures available.

Once the researchers fully understand the factors affecting the formation of nanotubes from aluminosilicogermanate materials, they hope to apply similar principles to other metal oxides. The ultimate goal will be an ability to predictably vary the dimensions of nanotubes – and potentially other useful nanostructures – employing different chemical process conditions across a broader range of metal oxide materials.

"One can get a large range of useful properties with metal oxide materials," Nair noted. "Almost all metals form oxides and many of them form layered sheet-like oxides, so if one can coax them into nanotube form with dimensions comparable to single-walled carbon nanotubes, the range of useful properties would be great."

Controlling the dimensions of nanostructures is critical because properties such as electronic band-gap depend strongly upon the dimensions. Dimension control has proven to be difficult in carbon nanotube fabrication processes, leading to an entire area of research focused on purifying nanotubes of specific dimensions from an initial mixture of different sizes.

“If we are able to produce single-walled nanotubes of specific and controllable diameter with inexpensive water-based chemistry, devices based on them would perform in a consistent and predictable manner,” Nair explained. “If we could synthesize the same nanotube structure with predictably different diameters and lengths, we can tune the properties like the band-gap across a wide range. We could even get a limited toolbox of materials to do many different things.”

Though the chemical reactions that produce the metal oxide nanotubes are complicated, they occur over a period of days at low temperatures and can be carried out with simple laboratory apparatus. That facilitates control over processing conditions and allows the researchers to track many different aspects of the reaction with a variety of characterization tools.

“There is a lot of complex chemistry that can be done in the aqueous phase, which motivated us to understand the processes by which metal ions dissolved in water organize themselves together with oxygen into specific nanotubular arrangements, perhaps aided by water and other species present in the solution,” Nair added.

The metal oxide nanotubes have properties very different from those of carbon nanotubes, which have been studied heavily since they were discovered in the 1990s. “For example, the materials that we are working with are much more hydrophilic than carbon and can load nearly 50 percent of their weight with water,” Nair explained. “There is a whole

range of behavior in oxide nanotubes that we cannot explore with carbon-based materials."

Source: Georgia Institute of Technology