Nanotubes line up to form films

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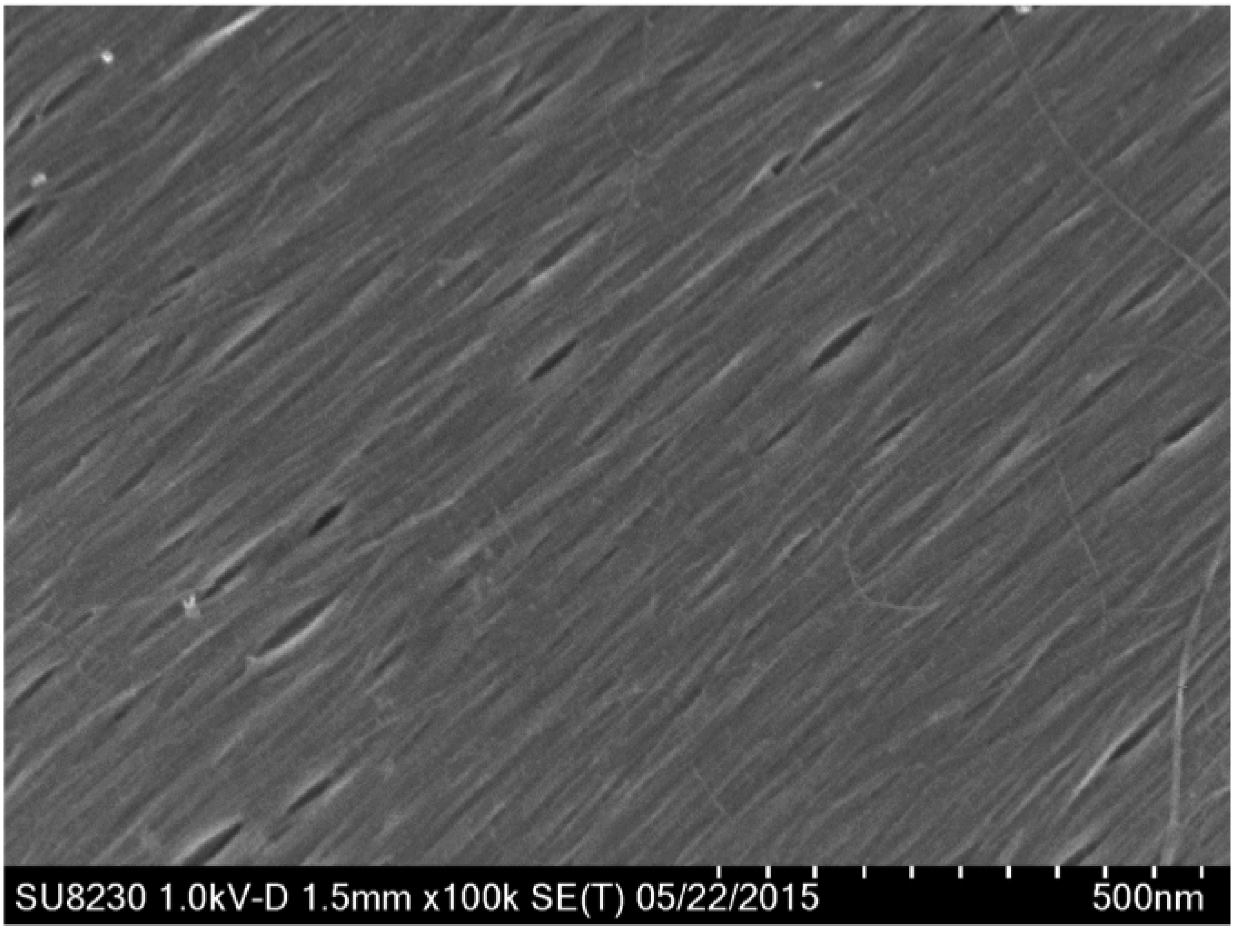

A scanning electron microscope image shows highly aligned and closely packed carbon nanotubes gathered into a film by researchers at Rice University. Credit: Kono Lab/Rice University

A simple filtration process helped Rice University researchers create flexible, wafer-scale films of highly aligned and closely packed carbon nanotubes.

Scientists at Rice, with support from Los Alamos National Laboratory, have made inch-wide films of densely packed, chirality-enriched single-walled carbon nanotubes through a process revealed today in *Nature Nanotechnology*.

In the right solution of nanotubes and under the right conditions, the tubes assemble themselves by the millions into long rows that are aligned better than once thought possible, the researchers reported.

The thin films offer possibilities for making flexible electronic and photonic (light-manipulating) devices, said Rice physicist Junichiro Kono, whose lab led the study. Think of a bendable computer chip, rather than a brittle silicon one, and the potential becomes clear, he said.

"Once we have centimeter-sized crystals consisting of single-chirality nanotubes, that's it," Kono said. "That's the holy grail for this field. For the last 20 years, people have been looking for this."

The Rice lab is closing in, he said, but the films reported in the current paper are "chirality-enriched" rather than single-chirality. A carbon nanotube is a cylinder of graphene, with its atoms arranged in hexagons. How the hexagons are turned sets the tube's chirality, and that determines its electronic properties. Some are semiconducting like silicon, and others are metallic conductors.

Rice University researchers discovered a method to make highly aligned nanotube films. The films may become valuable for flexible electronics and photonic devices. Credit: Jeff Fitlow/Rice University

A film of perfectly aligned, single-chirality nanotubes would have specific electronic properties. Controlling the chirality would allow for tunable films, Kono said, but nanotubes grow in batches of random types.

For now, the Rice researchers use a simple process developed at the National Institute of Standards and Technology to separate nanotubes by chirality. While not perfect, it was good enough to let the researchers make enriched films with nanotubes of different types and diameters and then make terahertz polarizers and electronic transistors.

The Rice lab discovered the filtration technique in late 2013 when graduate students and lead authors Xiaowei He and Weilu Gao inadvertently added a bit too much water to a nanotube-surfactant suspension before feeding it through a filter assisted by vacuum. (Surfactants keep nanotubes in a solution from clumping.)

The film that formed on the paper filter bore further investigation. "Weilu checked the film with a scanning electron microscope and saw something strange," He said. Rather than drop randomly onto the paper like pickup sticks, the nanotubes - millions of them - had come together in tight, aligned rows.

"That first picture gave us a clue we might have something totally different," He said. A year and more than 100 films later, the students and their colleagues had refined their technique to make nanotube wafers up to an inch wide (limited only by the size of their equipment) and of any thickness, from a few to hundreds of nanometers.

Further experiments revealed that each element mattered: the type of filter paper, the vacuum pressure and the concentration of nanotubes and surfactant. Nanotubes of any chirality and diameter worked, but each required adjustments to the other elements to optimize the alignment.

The films can be separated from the paper and washed and dried for use, the researchers said.

They suspect multiwalled carbon nanotubes and non-carbon nanotubes like boron nitride would work as well.

Co-author Wade Adams, a senior faculty fellow at Rice who specializes in polymer science, said the discovery is a step forward in a long quest for aligned structures.

"They formed what is called a monodomain in liquid crystal technology, in which all the rigid molecules line up in the same direction," Adams said. "It's astonishing. (The late Rice Nobel laureate) Rick Smalley and I worked very hard for years to make a single crystal of nanotubes, but these students have actually done it in a way neither of us ever imagined."

Why do the nanotubes line up? Kono said the team is still investigating the mechanics of nucleation—that is, how the first few nanotubes on the paper come together. "We think the nanotubes fall randomly at first, but they can still slide around on the paper," he said. "Van der Waals force brings them together, and they naturally seek their lowest-energy state, which is in alignment." Because the nanotubes vary in length, the researchers suspect the overhangs force other tubes to line up as they join the array.

The researchers found their completed films could be patterned with standard lithography techniques. That's yet another plus for manufacturers, said Kono, who started hearing buzz about the discovery months before the paper's release.

"I gave an invited talk about our work at a carbon nanotube conference, and many people are already trying to reproduce our results," he said. "I got so much enthusiastic response right after my talk. Everybody asked for the recipe."

More information: Xiaowei He et al. Wafer-scale monodomain films of spontaneously aligned single-walled carbon nanotubes, *Nature Nanotechnology* (2016). DOI: 10.1038/nnano.2016.44

Provided by Rice University