

## Multiwall Nanotubes Self-Assemble into Strong, Transparent, Conductive Sheets

Archaeological evidence suggests that humans discovered the art of spinning fibers into yarns as early as the New Stone Age about 10 000 years ago. The technology continues to evolve today as materials engineers develop durable, ultrafine, and exotic kinds of yarns and fabrics. Carbon nanotubes are among the most intriguing of materials that can form such textiles. Composed of graphite sheets that seamlessly wrap into long cylindrical tubes, and available in single-wall and multiwall flavors, nanotubes are stronger than steel, extremely stiff, chemically stable, and nearly perfect thermal and electrical conductors. The challenge is to transfer those microscopic properties of the individual molecules to bulk materials at macroscopic scales.

Researchers have been making nanotube fibers, ribbons, and sheets for the past five years, ever since the University of Bordeaux's Philippe Poulin and colleagues injected surfactant-dispersed nanotubes into a polymer-containing coagulation bath. The process produced gel fibers that they then dried to make nanotube-polymer composite fibers. Sheets of nanotubes have also been made in solution—typically by filtering the dispersed nanotubes in water and peeling off the layer once dried.

That protocol can, for instance, make 20-micron-thick, opaque “bucky paper” composed of bundles of nanotubes randomly oriented within the plane of the paper. But dry, solid-state processes can do the job as well. By squirting a mixture of ethanol and an iron catalyst into a hot furnace using a jet of hydrogen gas, Alan Windle and colleagues at the University of Cambridge in England created an aerogel—a smokey mixture of gas and nanotubes. Much like cotton candy that is wound into strands around a spindle, the aerogel can be spun into continuous nanotube fibers and ropes directly out of the hot reaction zone.

In the context of those developments, Ray Baughman from the University of Texas at Dallas and researchers from UT and Australia's Commonwealth Scientific and Industrial Research Organisation have devised their own remarkably simple and solvent-free method to form nanotube threads and sheets.<sup>1</sup> Last year, after growing a thick forest of multiwall carbon nanotubes using chemical vapor deposition on a catalyst-coated surface, Mei Zhang of Baughman's team noticed that she could tease out nanotube strands and then simultaneously draw and twist them into a 1- $\mu\text{m}$ -thick, highly conducting yarn. Twisting the drawn fiber increased its strength a thousandfold; the tensile strength measured nearly 500 MPa for thread diameters just 2% the thickness of a human hair.

But how to weave together those threads, absent a tiny enough loom? “Sometimes Nature is kind,” Baughman says, when relating his surprise on finding that the natural topol-

ogy of the nanotube forest effectively took care of lateral stability. Grown to roughly 300-microns high with tube diameters a mere 10 nm, the multiwall nanotubes have huge aspect ratios. Each nanotube in the forest becomes intermittently entwined with neighboring nanotubes along its length.

Those interconnections and the effect of weak van der Waals forces between nanotubes combine to mat the tubes together as individual strands are drawn out. Pulling from the edge of the forest using an adhesive strip uproots a row of millions of nanotubes. Those in turn are tangled with the

next row, which they pull out, and so on. Despite an areal density of less than 3  $\mu\text{g}/\text{cm}^2$ , the centimeter-wide sheets are self supporting. The electron micrograph images at left illustrate the effect: a self-assembled textile of aligned nanotube threads mechanically coupled together. What starts as a 300- $\mu\text{m}$ -high nanotube forest becomes an aerogel film about 20- $\mu\text{m}$  thick as the nanotubes are drawn lengthwise. Overlaying sheets oriented 45° to each other creates the 4-ply reinforced structure shown in the bottom image. Sheets stacked this way have strengths of about 175 MPa/(g/cm<sup>3</sup>), comparable to Mylar and Kapton film.

If the fibrous sheet is transferred to a surface and immersed in liquid, the density increases four hundredfold and surface tension shrinks the nanotubes to a 50-nm film that is transparent, stable, and conductive. The researchers hope to eventually replace their multiwall nanotube forests with millimeter-high single-walled ones—a daunting task, but one that may increase electrical conductivity. Vacuum-filtered, transparent disordered single-wall nanotube films currently have surface resistivities roughly 20 times lower than what the UT Dallas researchers now measure in their transparent sheets.

Meanwhile, Baughman and his group have demonstrated a host of applications: polarized

lamps and filters, flexible electrodes, low-noise sensors, artificial muscle, solar cells, organic light-emitting diodes on glass and plastic, and microwave welding of layers of Plexiglas by sandwiching nanotube sheets between them. To feed the myriad uses, Baughman's team can pull sheets as quickly as 7–10 meters per minute—comparable to a commercial-wool spinner's 20 meters per minute. The production rate then depends on how quickly one can replace catalysts and regrow the nanotube forest. That's typically a 10-minute job.

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### Reference

1. M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, R. H. Baughman, *Science* **309**, 1215 (2005).

