

NANOTUBES

Strong bundles

The mechanical properties of nanotube bundles are limited by the sliding of individual nanotubes across each other. Introducing crosslinks between the nanotubes by electron irradiation prevents sliding, and leads to dramatic improvements in strength.

PULICKEL M. AJAYAN is at the Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, USA.

e-mail: ajayan@rpi.edu

FLORIAN BANHART is at the Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany.

e-mail: Banhart@uni-mainz.de

Ever since single-walled carbon nanotubes were discovered a decade ago^{1,2}, they have been touted as the strongest structures known. The Young's modulus of a single-walled nanotube is nearly a terapascal³ (10^{12} N m⁻²), unsurpassed by any other material synthesized to date. But no one has yet been able to make use of this impressive credential to build a super-strong nanotube-based fibre or rope. The best macroscopic fibres made up of aligned single-walled nanotubes fall far short of the expected values — a Young's modulus of a mere 80 Gpa for the best fibres produced so far^{4,5}. Similarly, contrary to expectations, poor mechanical response is seen in polymer composites reinforced by single-walled nanotubes⁶. Andras Kis and colleagues have now shown that a huge increase of the bending modulus — which is equivalent to the Young's modulus for a homogeneous rope — can be achieved by irradiation of nanotube bundles with high-energy electrons⁷. The researchers observe a 30-fold increase in the bending modulus, which is almost 70% of the value observed for isolated single-walled nanotubes.

One fundamental problem in translating the wonderful mechanical properties of individual nanotubes into larger bundles comes from the nature of inter-tube bonding. The high axial strength and modulus of the nanotubes are severely compromised when they are packed into bundles, because the weak forces between the nanotubes allow them to slide easily past each other when loaded mechanically. The bending modulus of a carbon nanotube bundle (Fig. 1) strongly decreases with diameter. This is because the nanotubes in a large bundle act as a loose collection of perfect wires with atomically smooth surfaces, offering no resistance to slippage. Kis and colleagues offer a unique solution to this problem. The idea is to prevent the slippage of nanotubes by creating inter-tube links established through strong covalent bonds. The researchers exploit

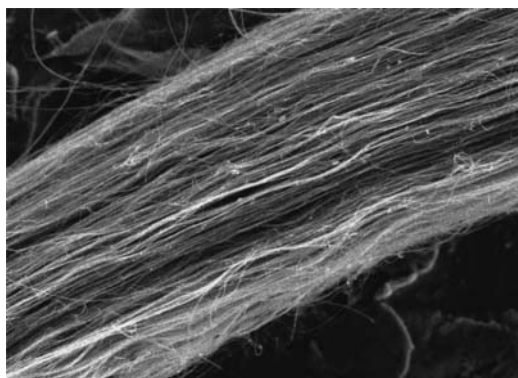


Figure 1 Large (ten micrometre diameter) bundle consisting of hundreds of aligned single-walled carbon nanotubes, synthesized by chemical vapour deposition¹². The mechanical properties of these large bundles are far inferior to what is experimentally observed for individual nanotubes.

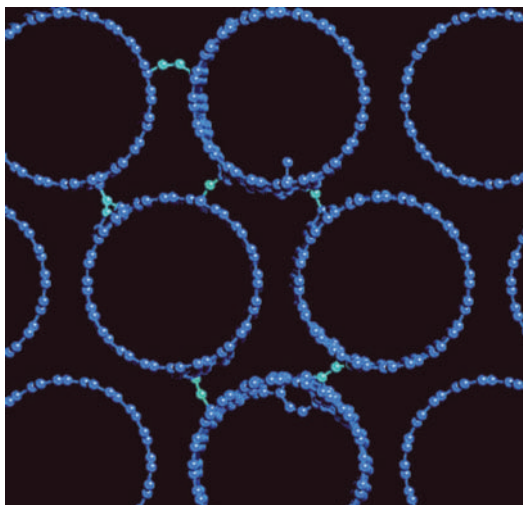
Reprinted with permission from Wei, B. Q. *et al. Nanoletters* 2, 1105–1107 (2002). Copyright (2002) American Chemical Society.

the sensitivity of carbon nanotubes to irradiation by using a high-energy electron beam to irradiate individual nanotube bundles in a transmission electron microscope. They then use an atomic force microscope to measure the bending modulus of the irradiated nanotube bundles.

In the nanotube lattice, each carbon atom forms bonds with three nearest neighbours. As the atoms are sp^2 -hybridized, the fourth electron of every atom is transferred into the π -electron system and is therefore not available for the formation of a covalent bond normal to the plane. However, if one or more carbon atoms are removed from the lattice, the situation changes. Let's consider two adjacent single-walled carbon nanotubes within a bundle, interacting by a weak van der Waals attraction. What happens if we start removing atoms from their lattices and place them in the interstitial space between the tubes? Contrary to naive expectation, the vacancies in the tubes do not just recombine with the mobile interstitial atoms. Instead, as Kis and colleagues show, two vacancies on adjacent tubes become linked by one or two interstitial atoms, generating a covalent bridge between the tubes. Due to the change in bonding angles close to the bridge, diamond-like sp^3 bonds form locally. Experimental and theoretical work presented in this study shows that these bridges are strong and stable and prevent the sliding of nanotubes against each other. The authors suggest that crosslinking could also result from irradiation-induced bonding between chemical moieties present on the nanotube surfaces (for example, carboxyl groups).

Figure 2 Simulation of ion-irradiated single-walled carbon nanotubes with bridges of carbon atoms (highlighted in green) between the tubes¹¹.

(Image courtesy of A. Krashennnikov).



Kis and colleagues achieved the removal of carbon atoms by irradiation with high-energy electrons, which is the 'cleanest' way of generating defects. The physics of electron–solid interactions is complex, but two basic mechanisms are important⁸. At electron energies below a threshold of around 85 keV (ref. 9), the energy is transferred to the electron system of the nanotube, and local excitation or bond breaking occurs. Above this threshold, atoms are displaced by knock-on collisions with the electrons, creating persistent interstitial-vacancy pairs and resultant structural damage. Kis *et al.* show that both processes contribute to the formation of crosslinks: the bending modulus of the bundle is increased by irradiation below as well as above the threshold electron energy. Surprisingly, the increase is substantially higher below the threshold, at 80 keV, where normally no irradiation-induced structural modification occurs.

This study should have significant impact on the processing of ultra-strong nanotube-based structures. Single-walled nanotubes synthesized in the laboratory are always in the form of bundles¹⁰, and exfoliation of these bundles to obtain individual nanotubes is difficult. Manipulation of individual tubes extracted from a bundle is also very challenging. The best strategy for producing nanotubes suitable for mechanical applications is by growing large aligned nanotube ropes (Fig. 1), crosslinked to extract the level of strength and stiffness available to individual nanotubes. This possibility is well demonstrated in the present study. Of course, large-scale processing of nanotube bundles by dedicated high-energy electron-beam sources could be tedious and expensive, and achieving precise control of the crosslink densities could be difficult. Alternatively, ions could be used as projectiles, as ion-beam sources are readily available. Simulations have already suggested that crosslinking of nanotubes within a bundle will occur under ion irradiation¹¹ (Fig. 2). The work by Kis and colleagues marks an important new step in resolving the inherent structural issue in nanotube assemblies, and paves the way towards realizing stronger nanotube fibres in the future.

References

1. Iijima, S. & Ichihashi, T. *Nature* **363**, 603–605 (1993).
2. Bethune, D. S. *et al.* *Nature* **363**, 605–607 (1993).
3. Treacy, M. M. J., Ebbesen, T. W. & Gibson, J. M. *Nature* **381**, 678–680 (1996).
4. Zhu, H. W. *et al.* *Science* **296**, 884–886 (2002).
5. Dalton, A. B. *et al.* *Nature* **423**, 703 (2003).
6. Ajayan, P. M., Schadler, L. S., Giannaris, C. & Rubio, A. *Adv. Mater.* **12**, 750–753 (2000).
7. Kis *et al.* *Nature Mater.* **3**, 153–157 (2004).
8. Banhart, F. *Rep. Progr. Phys.* **62**, 1181–1221 (1999).
9. Smith, B. W. & Luzzi, D. E. *J. Appl. Phys.* **90**, 3509–3515 (2001).
10. Thess, A. *et al.* *Science* **273**, 483–487 (1996).
11. Salonen, E., Krashennnikov, A. V. & Nordlund, K. *Nucl. Instr. Meth. Phys. Res. B* **193**, 603–608 (2002).
12. Wei, B. Q. *et al.* *Nanolett.* **2**, 1105–1107 (2002).

nature
materials

Call for correspondence

Nature Materials would like to give our readers the opportunity to discuss subjects that are of broad interest in the materials science and engineering community. We are therefore pleased to welcome contributions to our Correspondence section. This section will publish letters that can be either linked to primary research articles, editorials, commentaries and News and Views published in *Nature Materials*, or discuss other topics of widespread interest to the community. The emphasis is on brevity (less than 400 words), topicality and widespread interest, and the journal reserves the right to edit letters to highlight the most interesting aspects. References, if absolutely necessary, should be restricted to five or fewer. *Nature Materials* seeks to promote discussion of issues relevant to materials science research and invites insightful, provocative and polemical correspondence.

Correspondence should be addressed to the Editor at materials@nature.com

Please see our website for further details

(<http://www.nature.com/naturematerials/authors/types.html>)

