## NANOTUBES
Controlling conductance

Most of the outstanding properties of carbon nanotubes rely on them being almost atomically perfect, but the amount of imperfections, and the effect that they have on the tube properties, has, to date, been poorly understood. New work shows that even a very low concentration of missing atom-pairs in the nanotubes has a large effect on their electrical conductance.

Figure 1 AFM image of a carbon nanotube[4], and, below, a schematic of a segment of the nanotube with pairs of missing atoms forming defects (in red). The conductivity of a single nanotube along the tube length is measured by moving the AFM tip along the tube and acquiring current–voltage data at each point. By using Ar^{+}-ion irradiation to introduce pairs of missing atoms into the tube, the effect of defects on the nanotube resistivity has been quantitatively determined.
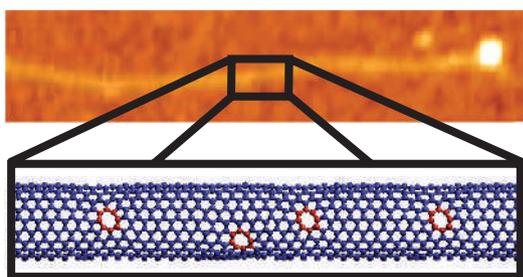
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Much of the initial attention on carbon nanotubes[1] was based on theoretical predictions of their expected unique properties. Single-walled tubes were predicted to be very strong, with tensile strengths up to 300 GPa, and were speculated to conduct electricity with fractionally charged collective modes (behaving as a so-called Tomonaga–Luttinger liquid)[2]. This expected high strength and conductivity naturally led to a rush in experimental studies of nanotube behaviour, and indeed, many of the expectations have now been confirmed. However, there are some exceptions: for instance, the strongest nanotubes so far synthesized have tensile strengths of about 60 GPa (ref. 3), much more than in conventional materials, but clearly significantly less than the first theoretical predictions. The issue of the mechanism of electrical conductivity remains unresolved, but appears to be much more complicated than initially thought. Now, Julio Gómez-Herrero and colleagues[4] have shown that a concentration of only 0.03% of missing atom-pairs in single-walled carbon nanotubes (SWNTs) produces a large decrease in their electrical conductance. This implies that to achieve optimal conductance properties the nanotubes must have very low concentrations of intrinsic defects, but also

suggests that irradiation could be used to obtain nanotubes of a desired resistivity.

One of the key reasons as to why some early theoretical predictions have not been corroborated is due to the presence of defects in the nanotube carbon network. It is crucial to understand the properties of these defects in order to conquer their detrimental effects, but also because controlled defect introduction may be used to tune nanotube properties in a desired direction. Recent work has shown that defect introduction using irradiation with high-energy electrons and ions can be used to modify the normally very weak interaction between nanotubes, and thus strengthen macroscopic nanotube materials[5,6].

Gómez-Herrero and colleagues have studied the electrical properties of metallic SWNTs that have been successively irradiated with Ar^{+} ions to produce a uniform density of defects (see Fig. 1). In everyday life, Ohm's law is valid, and the resistance of a wire increases linearly with its length L. The situation is different in nanoscale conductors such as nanotubes, where current is carried by individual conduction channels or modes, all having a resistance of 13 kΩ when the spin degrees of freedom are included. When there are no defects, the resistance is independent of length. However, when defects are present, localization effects emerge when the phase-coherence length of the electrons is larger than the 'localization length' L_0. This means that electronic wave functions cannot extend much further than distances of L_0. In this Anderson localization regime[7], disorder alone drives a system to an insulating state, and the resistance of the conductor is expected to increase exponentially as a function of the length.

By measuring the electrical resistance of the same metallic nanotube after successive irradiations, Gómez-Herrero and colleagues were able to plot the resistance as a function of the nanotube length — that is, the distance between the metal electrode and the metallic atomic force microscope (AFM) tip. They find that the resistance increases exponentially with length at scales $L \geq 500$ nm. The length scale at which this exponential behaviour is observed could be reduced substantially by irradiation with Ar^{+} ions, indicating that it is caused by Anderson localization.

The experiment takes advantage of the fact that the localization length in a carbon nanotube may

be very small. In the case of M conduction channels with interchannel coupling, the localization length is given by $L_{loc} \approx Ml$, where l is the mean free path. In a metallic SWNT with a mean free path of 100 nm, L_{loc} is only around 200 nm as $M = 2$. Consequently, the dephasing length can easily be longer than the localization length, which is the basic requirement for achieving Anderson localization.

It is interesting to note that in regular metallic conductors this kind of localized regime is impossible to achieve practically, as in a nanosized conductor with a cross section of 20×20 nm^2, the number of conduction modes is still 10^4 and, even if the mean free path l is as short as 1 nm, the localization length is about 10 μm. Contrary to the ambient conditions used in the nanotube experiments, in metallic systems one would need sub-Kelvin temperatures in order to have the dephasing length similar to the localization length. In this sense, even though being carried out at room temperature, the work of Gómez-Herrero and colleagues can be considered a fine zero-temperature measurement!

In the weakly localized regime, $L < L_{loc}$, the resistance is nearly a linear function of L. This allows a clear subtraction of contact resistance from the data and, thereby, a fitting of the data to the expected length dependence for Anderson localization. The experimental fits indicate that a disordered single-walled nanotube behaves in accordance with the Anderson-localization picture with interchannel

coupling, but not as independent, parallel quantum wires as one might expect on the basis of the strongly interacting models of perfect carbon nanotubes. Whether interaction effects — that is, Tomanaga–Luttinger-liquid type of correlations — play a role has to be resolved by future investigations.

The results are also interesting because they predict that a single missing atom (a vacancy) has only a weak effect on conductivity, but a pair of missing ones (a divacancy) has a strong one. A concentration of just 0.03% of divacancies produces an increase in the resistance of a 400-nm SWNT of three orders of magnitude. This implies that electron and light ion-irradiation might affect the conductivity less than heavy ion irradiation, because the latter kind produces more divacancies. Various kinds of irradiation could thus perhaps be useful for tuning nanotube resistivities to a desired value. Most importantly, the quantitative data provided by this work gives us an idea of how good the quality of the nanotubes should be to achieve optimal conductivity.

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MATERIAL WITNESS

In praise of wood

In his classic book *The New Science of Strong Materials*, soon to be reissued by Princeton University Press, Jim Gordon tells how, during his wartime work on aircraft materials, he would be regularly reminded by Charles Gurney, a specialist on fracture mechanics, that "Plastics are made by fools like me, but only God can make a tree."

"I found it depressing", Gordon wrote, "because wood was in fact a better material for making aeroplanes than the plastics which we could then produce."

I suspect that Gordon was also secretly a little pleased by that too. Trained as a naval architect and all his life an avid sailor, he clearly loved wood and found it a bountiful source of inspiration for his pioneering work on composites. He drew attention to the ingenious cross-winding of cellulose fibres in successive layers of the cell walls of wood, and was clearly delighted by the way it absorbed the energy of a propagating crack through a combination of buckling and fibre elongation — a process that Gordon's colleague George Jeronimidis at the University of Reading showed could account for wood's remarkably high work of fracture.

Weak interfaces, fibre orientation, laminar

and hierarchical structure: these are all tricks now well recognized in the field of biomimetic materials engineering, which Gordon foresaw long before its time. Add to that its biodegradability (although this is of course sometimes a drawback), light weight, low cost, mouldability and beautiful appearance, and it is hard to find a more versatile structural material than wood, which is why it is still used today in applications ranging from musical instruments to construction scaffolding.

It is all the more striking, then, that convention tends to confine discussions of biopolymers to proteins and nucleic acids, ignoring carbohydrates. This is largely because the former two polymers are where biological information — crudely, the software of the cell — primarily resides, making them of greatest relevance to biological function and biomedical intervention. But it by no means follows that carbohydrates are uninteresting or simple — indeed, it is probably fair to say that their relative neglect comes about because they are so hard both to understand and to synthesize. Many of the microstructural and molecular details of crystalline, amorphous

and liquid-crystalline cellulose remain to be uncovered. Glycopeptides are evidently crucial players in the specificity of biochemical reactions (and thus of great interest for drug development), but the chemistry of their synthesis has only recently become a hot topic.

For the materials scientist, the potential of cellulose is tremendous, as a new review illustrates (D. Klemm *et al. Angew. Chem. Int. Edn* **44,** 3358; 2005). Plasticized cellulose nitrate (celluloid) was of course one of the first industrial (semi-)synthetic polymers, and cellulose derivatives are used in coatings, laminates, pharmaceuticals, foods and textiles. Cellulose is a versatile framework for supramolecular chemistry, and it is now produced by bacterial fermentation as a fabric for tissue engineering and a tough, 'green' form of paper. There is plenty still to discover and celebrate in cellulose.

Philip Ball
(Winner of the Aventis prize for Science Books, 2005)