NANOTUBE SYNTHESIS

Cloning carbon

Most methods for making carbon nanotubes require further processing to separate tubes based on chirality. Now, seeding growth from an existing nanotube segment ties synthesis and selectivity into a single step.

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If you cut a worm in half, will you end up with two? Children know the empirical answer to this question: if divided in the right place, the halves can regenerate themselves. Picture a similar process for carbon nanotubes — the proposed workhorse for many nanotechnology devices — and you have the basic concept that scientists at Rice University are using to grow nanotubes with predefined diameters and electronic properties. Starting from a nanotube segment, and promoting catalytic growth at both ends, James Tour and co-workers ‘amplify’ the segment to create a longer version of the original.

Whether single-walled carbon nanotubes (SWNTs) will meet existing expectations for applications in nanoelectronics will ultimately depend on how well the key structural and electronic parameters can be controlled. Chirality, which describes how the nanotube is conceptually rolled from a graphene sheet and is defined by the indices (n,m), uniquely determines the diameter and whether the nanotube is semiconducting or metallic. Therefore the ability to reproduce nanotubes with exactly the same chirality is essential for the viability of nanotube transistors.

Ever since the first report of carbon nanotube synthesis by Iijima, an intensive effort has been focused on separating nanotubes according to size and type. One of the first successful separation methods was to apply a high bias voltage across a bundle of SWNTs. Metallic tubes will pass a large current, burning up in the process, whereas semiconducting tubes remain intact. An alternative method is to take advantage of the different chemistry of semiconducting and metallic nanotubes. Certain chemicals will only bond to metallic tubes making them heavier than their semiconducting counterparts and therefore easily separable. Yet another technique is alternating current dielectropheresis, which differentiates semiconducting and metallic materials in solvents by their dielectric constants.

However, although all these techniques can separate semiconducting from metallic tubes, many are not selective for the diameter and chirality. Furthermore, techniques such as chemical functionalization may introduce defects and require further processing to restore the useful electronic properties of the nanotubes. For nanotransistor applications, better techniques are still in demand.

An altogether different approach is to combine synthesis and selectivity into a single step. One way to do this is to ‘seed’ the growth of a nanotube from another nanotube or carbon structure. In our group, for example, we proposed to seed a single nanotube from the rim of a geodesic carbon dome with controlled radius and carbon arrangement. For a batch of domes that have the same number of carbon atoms and arrangement, the final diameter and chirality of all the SWNTs should in principle be the same.

The approach by Tour et al is similar and builds on a concept first proposed and tested by Richard Smalley. Instead of using a carbon dome, they seed nanotube growth from short segments of an existing SWNT with well-defined diameter and chirality. The SWNTs are deposited horizontally on the oxidized surface of a silicon substrate. A catalyst nanoparticle, such as Fe(NO3)3, is attached to each open end of the short segment by wet chemistry. When the particles are annealed in hydrogen, the Fe(NO3)3 reduces to Fe, a common catalyst for nanotube synthesis (Fig. 1a). Each Fe nanoparticle serves as a catalyst site for nanotube growth — in this case via the vapour–liquid–solid growth mechanism — when ethylene (C2H4) is introduced at high temperature as the carbon source.

The nanotube segments are thus ‘amplified’ at each end, growing as much as a few micrometres in length. A topographic atomic force microscope (AFM) image of an as-grown tube shows that the height is constant from the seed to the amplified...
end, suggesting a single diameter. Based on this result, the authors also conclude that the amplified SWNTs have the same predetermined chirality as the seeds.

There is no doubt that the work by Tour et al. will be important in moving the field of SWNT synthesis with controlled diameter and chirality forward. Moreover, it will likely have a positive influence on research focused on SWNT nanotransistors, particularly if the process can be scaled to a much larger volume. However, there are some caveats. First, definitive proof that the process yields control over the diameter and chirality has yet to be firmly demonstrated. What the authors can say for certain is that the short SWNT seeds grow in both directions and the AFM height profiles are consistent with the amplified ends having the same diameter as the seed. However, it is not always possible to assume that two segments with the same diameter will have the same chirality. For example, a (9,0) zigzag metallic nanotube has a diameter of 0.705 nm, whereas a (7,3) chiral semiconducting nanotube has a diameter of 0.696 nm (the diameter is proportional to \(\sqrt{n^2 + mn + m^2}\)). Such a small diameter difference (less than 1.3%) cannot be resolved by AFM height profiling alone. A better way to provide the pivotal information on both the diameter and chirality of the elongated nanotube sections is to measure either the Raman shift, which gives a more precise measure of diameter, or to image the atomic arrangement from seed to amplified end with scanning tunnelling microscopy (Fig. 1b)

In addition, the yield of the process—defined as the percentage of segments that seeded nanotube growth from both ends — is only about 3%. It is therefore a concern that the nanotubes may grow from free catalyst particles on the silicon substrate rather than from the short SWNTs. In order to further prove their claims, it will be necessary to demonstrate that there is absolutely no growth when short SWNT seeds are absent and all other conditions remain unchanged, and to improve the yield to a much higher level.

Even though the work by Tour et al. is still in the preliminary stages, the results do point in a promising direction. I am confident that, sooner or later, it will be possible to synthesize SWNTs with any diameter and chirality in large quantities and with any luck, this will happen just in time to operate the first nanotube-based computer.

References