Do single-walled carbon nanotubes occur naturally?

To the Editor — Although it is generally assumed that carbon nanotubes are naturally occurring, there is surprisingly little evidence to support this assumption[1]. Transmission electron microscope (TEM) images of what appear to be multiwalled carbon nanotubes (MWNTs) isolated from a Greenland ice core have been published[2], as have images of hollow carbon fibres from oil-well samples[3], although there remain questions about the validity of this evidence owing to the lack of clear high-resolution TEM images, high-quality diffraction patterns or Raman spectroscopy data. However, we are unaware of any evidence proving that single-walled nanotubes (SWNTs) can be synthesized by nature. This may appear a mere curiosity, but there is actually a pressing need to answer this question: the issue of patent validity.

There has been enormous growth in patents related to carbon nanotubes, fuelled by predictions that the market for nanotubes will be $9 billion by 2020[4]. Between 1994 and 2006 it was estimated that 1,865 nanotube-related patents were issued in the US, and last year it was reported that "in the past 3 years the number of CNT-related issued patents has almost tripled. For patents pending … a cumulative backlog close to 4,500 applications"[5]. Despite this, any application specifically seeking to patent a carbon nanotube structure (that is, composition of matter claims), may be voided if carbon nanotubes are shown to be naturally occurring, as outlined in Diamond versus Chakrabarty[6]: "the laws of nature, physical phenomena, and abstract ideas have been held not patentable … thus, a new mineral discovered in the earth or a new plant found in the wild is not patentable subject matter."

The legal requirements for 'natural occurrence' stipulate that the SWNT must occur spontaneously in nature: that is, it must self-assemble without any assistance from 'man'. Unquestionably, a SWNT forms spontaneously because its structure represents a low-energy configuration, and hence one favoured by nature, for a given number of carbon atoms[7]. However there is no published evidence to suggest this actually occurs without assistance.

This lack of evidence may simply be due to the inherent difficultly in observing SWNTs in samples isolated from natural environments. None of the mainstream SWNT detection methods (for example, electron microscopy or Raman spectroscopy) are capable of rapidly screening large numbers of 'natural' samples for SWNTs. In any case the results are difficult to apply given the lack of any legal definition for a carbon nanotube[1]. Hence, randomly testing natural samples for the presence of SWNTs may never yield conclusive evidence.

Should the discovery of naturally occurring SWNTs turn out to be a practical impossibility, the courts will be required to adjudicate solely on the basis of theory. This is also problematic, given that it remains unclear whether SWNTs and MWNTs form via the same mechanism. It is also unclear whether the various methods used to produce carbon nanotubes are mechanistically consistent[8].

The most likely growth mechanism for SWNTs in nature is the transformation of another carbon structure, or the chemical vapour deposition (CVD) of a carbon feedstock under appropriate conditions (conditions similar to those of arc discharge synthesis could also potentially be created by lightning strikes). For the transformation pathway, fullerenes are known to be a suitable carbon source for MWNT growth under certain conditions[9]. The abundance of naturally occurring fullerenes in carbon materials (for example, coal, rocks, interstellar media and even dinosaur eggs[10]) therefore suggests a possible route for SWNTs to form in nature.

In laboratory-based CVD, a gaseous carbon source is dehydrogenated to form the nanotubes, generally at temperatures between 500 and 1,000 °C, in the presence of a catalyst. In a discussion of growth mechanisms that are potentially applicable to CVD, Charlier and Iijima[7] suggested that MWNTs could be formed from a SWNT 'nucleus', followed by tube 'thickening' to produce additional walls. This means that if MWNTs occur naturally, then SWNTs might also occur naturally, but without any evidence being left behind because they act as precursors for MWNTs formation.

However, it remains possible that SWNTs do not form naturally. It is widely acknowledged that SWNTs form under a narrower range of conditions than MWNTs[7] and hence it is possible that nature does not provide for these more stringent requirements. In the event of interruptions to the supply of carbon or fluctuations in the growth pressure or temperature, for example, the growing SWNT may prematurely cap, forming a fullerene to minimize structural energy. The abundance of naturally occurring fullerenes suggests this may be a dominant natural outcome, thus preventing SWNTs from forming. In most instances, the artificial synthesis of SWNTs also requires the use of small (<5 nm) metallic particles to act as a catalyst[7]. This extra requirement — over and above the need for elevated temperatures and a suitable carbon source, among other prerequisites — might simply mean there are no naturally occurring locations that are conducive to SWNT growth.

The issue of the natural occurrence of carbon nanotubes may initially appear trivial, but it is likely to feature in legal discussions about the merits of many nanotube-related patents. Although many fundamental nanotube patents are approaching their expiry date (for example, US Patent 5424054 "Carbon fibers and method for their production", which is held by IBM, is due to expire in 2013, and US Patent 5747161 "Graphite filaments having tubular structure and method of forming the same", which is held by NEC, will expire in 2016), ever-increasing nanotube production volumes heighten the likelihood of litigation from patent holders. Consequently the question of natural occurrence may still have substantial financial implications should the market for nanotubes grow as predicted. In the absence of any physical evidence for naturally occurring SWNTs, at the very least there must be a universally accepted growth mechanism available to the courts to determine the likelihood of natural SWNT occurrence.

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