

Guest Editorial

Who should be given the credit for the discovery of carbon nanotubes?

Carbon nanotubes play a large part in manuscript topics submitted to CARBON and, of course, to many other journals in almost every field of research and technology. Many of them start with referring to “*the discovery of carbon nanotubes by Iijima in 1991...*”. Such a recurrent sentence makes a statement which is misleading, often wrong, and neglectful of the scientists who preceded this citation on the path to understanding carbon materials. A former Editor of CARBON, H.P. Boehm, raised this question some years ago [1], however it has unfortunately received little attention. Fifteen years after carbon nanotubes suddenly supplanted fullerenes as the hottest research topic of the Twentieth Century, we consider it time to provide a clear picture of who should really be given the credit for the discovery of carbon nanotubes. We have here a double goal: inform young scientists who believe that the nanotube story started in the nineties, and thus (hopefully) make the work of the Editors easier.

In carbon nanotube history, single-walled (SWCNT) should be distinguished from multi-walled (MWCNT). It is perfectly clear that the formation of SWCNTs was first reported in the June 17th issue of NATURE in 1993 by two papers submitted independently, one by Iijima and Ichihashi [2], at the time affiliated at NEC, the other by Bethune et al. from IBM, California [3]. If prior claim is a major issue, then it should go to the Japanese team since they submitted their paper on April 23rd, as opposed to May 24th for the US team. But we all know that experimental research is not a one-day thing, and determining who made the first discovery would need to be confirmed by investigating both laboratory records. Besides, we must remember that the discovery was incidental in both cases, since SWCNTs were formed in failed attempts to produce MWCNTs filled with transition metals. From a scientific point of view (which may be different from proprietary right issues), it is not worth the trouble, and it appears fair to acknowledge the credit for the discovery of SWCNTs to both teams. A possibly controversial image can, however, be found in a figure from a paper published in 1976 by Oberlin et al. [4] showing a nanotube resembling a

SWCNT, though not claimed to be so by the authors (Fig. 1, between the arrows).

Unfortunately, the magnification used did not allow graphene fringes to be resolved so that the number of walls cannot be determined. However, considering the diameter of this tube (~5 nm) and what is expected from calculations of the energetic stability of a SWCNT [5], it is unlikely that a nanotube with such a large diameter be single-walled. It is correct that, in contradiction to calculations, large diameter SWCNTs are sometimes experimentally reported in the literature, but they generally originate from peculiar synthesis conditions (such as plasma-enhanced CVD) instead of regular catalysis-enhanced CVD as used in [4]. In any event nobody has claimed that the nanotube shown in Fig. 1 was SWCNT type. Indeed, nobody from the carbon material community at that time was ready to admit that nanotubes built up using a rolled single graphene could ever exist. Was it the first double wall carbon nanotube ever imaged? We will never know.

Problems start when considering MWCNTs. There is no doubt that the work on MWCNTs was boosted by the report made by Iijima in 1991 [6] on their occurrence in the hard deposit growing at the cathode during electric arc experiments to produce fullerenes. Actually, this paper is the first unambiguous evidence for the possibility of growing carbon nanotubes without the need of any catalyst (not considering the graphite whiskers formed by Bacon and Bowman in high pressure electric arc conditions [7], because they were not nanometer size). This should however not detract from the huge – yes, that is the word – amount of work carried-out before then, at a time where science was not yet into the nano-fashion.

The first mention of the possibility of forming carbon filaments from the thermal decomposition of gaseous hydrocarbon (methane) was reported in 1889 [8] – i.e., literally two centuries ago! – in a patent that proposed the use of such filaments in the light bulbs that had just been presented by Edison at the Paris Universal Exposition the same year. Other early reports consist of two papers presented at the French Academy of Sciences [9,10]. However,

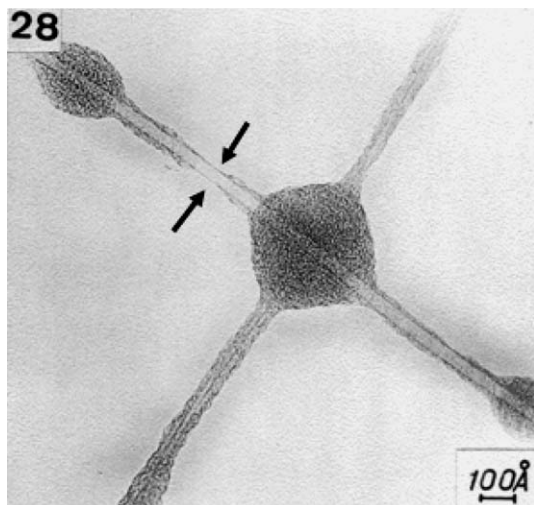


Fig. 1. TEM image of what could be a SWCNT specifically from the bare part between arrows, yet unlikely. This image was scanned from Endo's original thesis but a similar one was published in [4].

such papers can hardly be considered as the first evidence for the growth of carbon nanotubes since the resolution of the available microscopy tools (optical microscopes) were barely able to image filaments smaller than few micrometers in diameter, and definitely not able to reveal whether they had a sub-micrometer inner cavity. They are, however, directly related to our purpose since they demonstrated that thick vapour-grown carbon filaments were produced that we now know result from a two-step mechanism, the first corresponding to the catalysed growth of a nanotube, the second corresponding to a thickening step via a catalyst-free pyrolytic carbon deposition mechanism [11]. Thanks to the subsequent invention of the transmission electron microscope (TEM), the first commercial versions of which were produced by Siemens in 1939, significant progress was made in the fifties regarding the morphology and inner texture of carbon filaments. The first TEM evidence for the tubular nature of some nano-sized carbon filaments is believed to have appeared in 1952 in the *Journal of Physical Chemistry of Russia* [12], which may explain why the related papers are not well known and cited. Due to the cold war, access to Russian scientific publications for Western scientists was not easy at that time, and the use of the Russian language was pretty discouraging anyway! Also, many Russian-written papers were not mentioned in literature databases such as Current Contents. Figures from [12] clearly show carbon filaments exhibiting a continuous inner cavity, thereby forming tubes. Despite the fact that there is no scale bar, the indicated magnification value allows one to calculate (from the original journal issue) that the diameters of the carbon tubes imaged are in the range of 50 nm, i.e., definitely nano-sized. This is consistent with their perfect electron transparency in-between the dark contrast representing the tube walls (Fig. 2). Besides, the nanotubes imaged are obviously of MWCNT type, with walls being made up

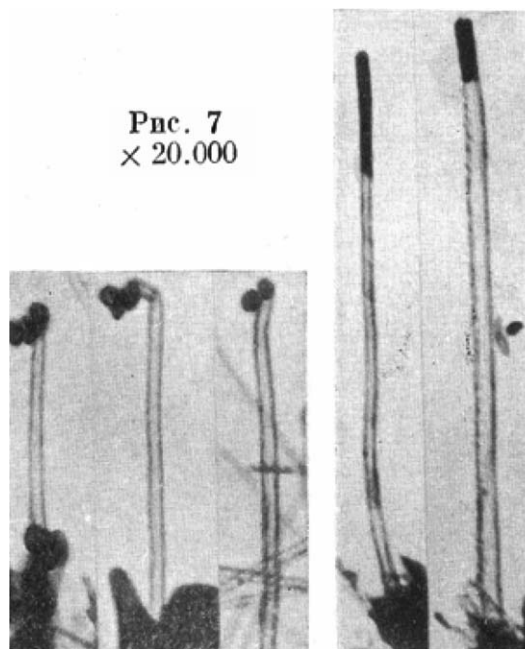


Fig. 2. Examples of TEM images of carbon nanotubes published in [12] (reprinted by permission of Nauka Publishers).

from 15 to 20 graphenes, assuming a concentric texture (which cannot be ascertained).

Many other reports then followed in papers that appeared in several journals including *CARBON*, by many authors who include great names in carbon science such as Baird, Baker, Boehm, Endo, Harris, Oberlin, Robertson, Walker, etc. It is not the purpose here to provide an exhaustive list of all the papers published in the field and to discuss their respective input. There is certainly room for a review paper on the subject. The fact is, Radushkevich and Lukyanovich [12] should be credited for the discovery that carbon filaments could be hollow and have a nanometer-size diameter, that is to say for the discovery of carbon nanotubes.

At that time the arrangement of graphenes in the nanotube walls could not be distinguished because TEM resolution was only in the nanometer range. Ascertaining when the various MWCNT textures (concentric, herringbone, bamboo, platelet) were determined is of minor importance, but most of them were deduced quite early from diffraction studies. For instance, in 1958, Hillert and Lange [13] reported carbon nanotubes exhibiting the concentric texture (determined from electron diffraction) and others exhibiting the bamboo texture (from imaging), along with examples of peculiar morphologies that are nowadays popular such as branched nanotubes, and coiled nanotubes. But the matter was debated until the seventies [14], i.e., until TEMs had sufficient resolution.

An intriguing question remains. Why did the scientific community seem to discover carbon nanotubes in 1991 when they had actually been known for forty years. It is true that vapour-grown carbon filaments have always been

the object of recurrent interest. In 1958 Hillert and Lange noted that “*Filamentary growth of graphite... has recently been discovered again, ...*” [13]; 15 years later, Baker et al. [15] similarly noted that “*Interest in catalytic decomposition of hydrocarbons on metallic surfaces...*” (i.e., which produced carbon nano-filaments) “*...has recently become more active*”. But none of these recurrent “rediscoveries” of the interest of carbon filaments reached the impact of the 1991 Iijima paper in NATURE [6]. There are many reasons for this. One is that carbon filaments and nanotubes have long been investigated by material scientists, whose main goal was to understand the growth mechanisms so that they could prevent their formation in coal and steel industry processing and in the coolant channels of nuclear reactors. Nothing so exciting for fundamental physicists! In addition, these scientists were often not readers of the materials and chemistry oriented journals – such as CARBON – in which the related studies were reported. The second reason is more general, and has to do with the level of maturity of science (which results from the combination of a set of favourable conditions, e.g., having the right materials available, as well as the related theory, investigation tools, scientific minds, ...) which was unable to really think “nano”. Hence, the undoubted tremendous impact of the 1991 Iijima paper came from the right combination of favourable factors: a high quality paper, a top-rank journal read by all kinds of scientists, including those involved in basic research and fundamental physics, a boost received from its relation to the earlier worldwide research hit (fullerenes), and a fully mature scientific audience ready to surf on the “nano” wave.

A final word. We believe the prior claim pointed out here to be the ultimate one. But the world is vast and literature is abundant. Should any reader be aware of published work that contradicts our statements, please let us know. If confirmed, it will be advertised, in the name of truth and for the benefit of all.

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