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Mini review: Synthesis of carbon nanotube

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Abstract: **Carbon nanostructures like fullerenes, graphene and nanotubes are of great interest for the current research as well as for future industrial applications. Carbon nanotubes (CNTs) have been under scientific investigation for more than fifteen years because of their unique properties that predestine them for many potential applications. The field of nanotechnology and nanoscience push their investigation forward to produce CNTs with suitable parameters for future applications. It is evident that new approaches of their synthesis need to be developed and optimized. The challenge on carbon nanotubes is still the subject of many research groups. While in the first years the focus was on the new synthesis methods, new carbon sources and support materials, recently, the application possibilities are the principal arguments of the studies. Moreover, the carbon nanotubes market is steadily growing and thus effective and cheap solutions for the production of high quality carbon nanotubes are needed. To the best of my knowledge, the main focus in the current research lays on exploring the effective production methods for singlewalled carbon nanotubes (SWNTs) because of their unique physical and chemical properties and hence their potential electronic application. In this paper we review history, types, structure and especially the different synthesis methods for CNTs preparation including arc discharge, laser ablation and chemical vapour deposition. Moreover, we mention some rarely used ways of arc discharge deposition which involves arc discharge in liquid solutions in contrary to standard used deposition in a gas atmosphere. This paper presents different synthesis methods like arc discharge (AD), laser ablation, chemical vapour deposition (CVD) as well as some of the more recent methods working with high pressure of the carbon monoxide of some unique catalytic mixture. The production methods are explained and their advantages and disadvantages examined. Although this paper concentrates on the synthesis, the other factors should not be completely neglected as they contribute significantly to the production costs.**

Keywords: **Carbon nanotube , laser ablation, chemical vapour deposition (CVD), arc discharge (AD).**

1. INTRODUCTION

Carbon nanotubes were discovered by Iijima in 1991 [1]. He analyzed the samples produced by arc discharge in He atmosphere. With TEM microscopy he observed some interesting hollow tubule-like structures with nanosized diameter. Since this time these structures called carbon nanotubes made long way, but they are still in the focus of research groups dealing with different fields of science. However, the first reports about these hollow nanosized tubules were made by Russian researchers in the middle of 50‘s and later on by Endo and co-workers [2,3]. Carbon nanotubes (CNTs) are characterized as a graphene sheet rolled-up to form a tube, for example a single-walled tube (SWNT). When two or more concentric tubes are placed one into another, multi-walled carbon nanotube (MWNT) is formed. Initially, the arc discharge was employed to produce carbon nanotubes. This method was known enough and utilized for the synthesis of carbon filaments and fibres. Later on other techniques such as laser ablation or chemical vapour deposition (CVD) were examined in the production of carbon nanotubes. In fact, these are the three main production methods. Some efforts were also made to look for other possibilities to grow nanotubes but they had less success. The cause may be the expensive reaction apparatus, the state or the price of the catalyst material, the strange reaction conditions, e.g., high pressure, temperatures of liquid nitrogen. So, the old technologies were improved, adapted to new conditions more than to discover new technologies. Today, the arc discharge and chemical vapour deposition methods are widly applied for the formation of carbon nanotubes. Many studies were made to improve either the quality or the quantity of the produced material by optimizing the synthesis process. During the challenge of the wonderful world of carbon nanotubes theoretical studies were also carried out. Their argument is the growth mechanism [4–6] of carbon nanotubes and the possibility of the formation of other nanostructures. It is supposed that the growth mechanism varies slightly from one type of production

method to another. It would be nice to discover the key parameters for their formation. Recently, the research is focused on the application possibilities of carbon nanotubes. Gratefully to their peculiar properties the field of applications is broad and it is opened from electronics, electromagnetic devices, to composite materials and optics, to biomaterials and biomedical devices. Studies in biological and pharmaceutical fields were given where carbon nanotubes can act as a part of biosensors, drug and vaccine delivery vehicles [7–13]. The important role of the synthesis parameters which were demonstrated to be key factors during the growth process is also outlined. The results summarized in this work are essentially the studies from the last decade.

1.1 Growth Mechanism

To begin with, I shortly explain the general growth mechanism of carbon nanotubes that is basically common for different growth methods. First of all, the exact way in which nanotubes are formed is not completely understood. One distinguishes between extrusion or tip-growth, and base-growth, which are both a three-step process. As schematically sketched in Fig.1, first, a round or pear-shaped precursor for the formation of nanotubes is formed on the surface of the metal catalyst. Second, the carbon diffuses on the sides of the precursor leaving, however, the top of it free – that is the reason for the hollow core of the nanotube. Out of this a rod-like carbon structure is formed. By the base growth (extrusion) the nanotube grows upwards from the metal particle that remains attached to the substrate. By the tip growth the particle detaches and stays on the top of the growing nanotube. Depending on the size of the catalyst particles, singlewalled or multi-walled nanotubes are grown.

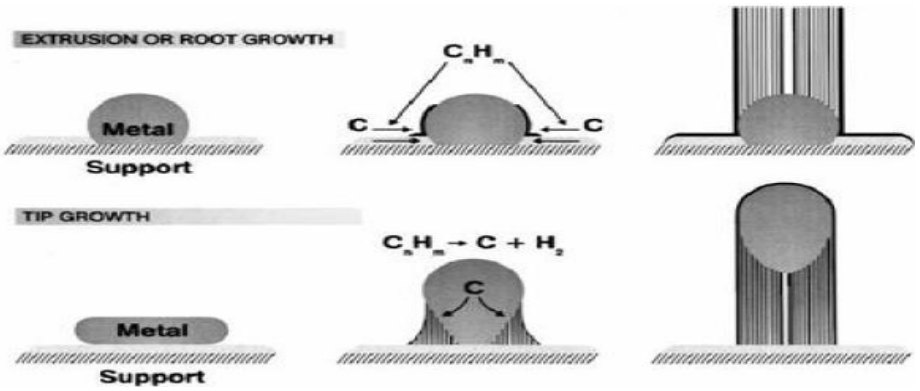

Fig 1: Extrusion or root growth

2. ARC DISCHARGE AND LASER ABLATION:

The two methods that are schematically sketched in Fig.2 and Fig.3 share some similarities both in their working principle and in the pros and cons of the production. During the arc discharge, that for the carbon nanotubes was firstly used by Sumio Iijima in 1991 [1], two graphite rods are placed in an enclosure that is filled with some inert gas (like helium or argon) at low pressure (between 50 and 700 mbar). The carbon rods act as electrodes which are kept at different potentials. The anode is moved close to the cathode until an arc appears and the electrodes are kept at the distance of 1 mm for the whole duration of the process that takes about one minute. After the de-pressurisation and cooling of the chamber the nanotubes together with the by-products, can be collected. Most nanotubes deposit on the cathode. The synthesis product yield which represents the amount of carbon nanotubes expected in the converted carbon is 60% [14]. In 1995 Richard E. Smalley and his group used for the first time laser ablation to grow high quality nanotubes. Intense laser pulses ablate a carbon target which is placed in a tube-furnace (Fig. 3) heated to 1200°C [15]. During the process some inert gas like helium or argon flows through the chamber to carry the grown nanotubes to the copper collector. After the cooling of the chamber the nanotubes and the by-products, like fullerenes and amorphous carbon over-coating on the sidewalls of nanotubes can be collected. The use of pure carbon leads for both methods to the synthesis of multi-walled nanotubes and the addition of a catalyst like iron, yttrium, sulphur, nickel and molybdenum leads to the formation of the single-walled carbon nanotubes [16]. As the temperatures involved in these methods are very high, e.g. up to 4000°C for the arc discharge, approximately 28% of the carbon anode evaporates [14]. Nowadays these methods are almost not used any more for the synthesis. The reasons for it are: the very high temperatures involved, the consequent evaporation of the carbon source, the highly tangled, and disordered nanotubes resulting. Moreover, no structure, pattering or substrate growth is possible; due to the short process times only synthesis of the short nanotubes is possible. In addition to that, the amount of the purification needed is very high. In order to address this issues other methods were developed.

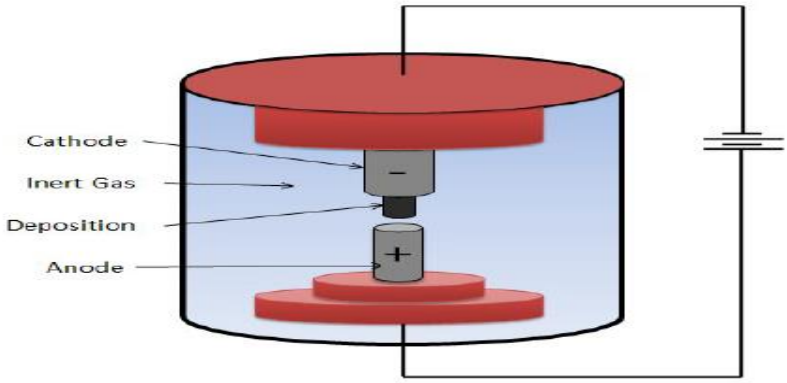

Fig 2: Arc discharge

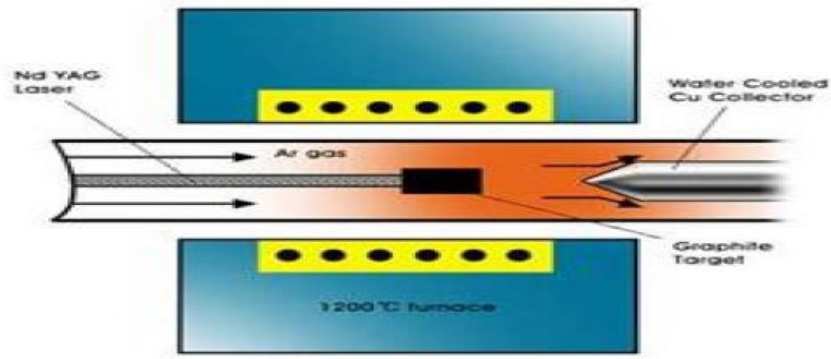

Fig 3: Laser ablation

2.1 Production of single-walled nanotubes by arc-evaporation:

The discovery of single-walled carbon nanotubes, like so many in fullerene science, was serendipitous. In early 1993, several groups reported that foreign materials could be encapsulated inside carbon nanoparticles or nanotubes by carrying out arc-evaporation using modified electrodes. Rodney Ruoff's group in the USA [17]and Yahachi Saito's group in Japan [18]prepared encapsulated crystals of LaC2 by employing electrodes impregnated with La, while Supapan Seraphin and colleagues reported that YC2 could be introduced into nanotubes by using electrodes containing Y [19]. This work opened the way to a whole new field based on the use of nanoparticles and nanotubes as 'molecular containers', but it also led indirectly to a quite different discovery, with even more important implications. Donald Bethune and his colleagues of the IBM Almaden Research Center in San Jose, California were particularly interested in the papers of Ruoff and others. This group were working on magnetic materials for applications in information storage, and believed that ferromagnetic transition metal crystallites encapsulated in carbon shells might be of great value in this area. Bethune therefore set out to try some arc-evaporation experiments using electrodes impregnated with the ferromagnetic transition metals Fe, Co and Ni and an atmosphere of He (100–500 torr), but the result of this experiment was not at all what he expected. To begin with, the soot produced by arc-evaporation was quite unlike the normal material produced by the arc-evaporation of pure graphite. Sheets of soot hung like cobwebs from the chamber walls, while the material deposited on the walls themselves had a rubbery texture, and could be peeled away in strips. When Bethune and his colleague Robert Beyers examined this strange new material using high-resolution electron microscopy they were astonished to find that it contained multitudes of nanotubes with single-atomic-layer walls. These ultra-fine tubes were entangled with amorphous soot and particles of metal or metal carbide, holding the material together in a way that would account for its strange texture. This work was written up for Nature and appeared in June 1993 [20]. Micrographs taken from their paper are shown in Fig. 4. Independently of the American group, Sumio Iijima and Toshinari Ichihashi of the NEC laboratories in Japan were also experimenting with arc-evaporation using modified electrodes. In addition, they were interested in the effect of varying the atmosphere inside the arc-evaporation chamber. Like Bethune and colleagues, they discovered that certain conditions produced a quite different type of soot from that normally formed by arc-evaporation. For this work, the Japanese

researchers impregnated their electrodes with Fe, and the atmosphere in the arc-evaporation chamber was a mixture of methane and argon rather than pure He. When examined by high-resolution electron microscopy, the arc-evaporated material was found to contain extremely fine single-walled nanotubes running like threads between clusters containing amorphous carbon and metal particles [21]. Single-walled nanotubes differ from multiwalled tubes produced by conventional arc-evaporation in having a very narrow range of diameters. In the case of the multiwalled tubes, the inner diameter can range from c. 1.5 to c. 15.0 nm, and the outer diameter from c. 2.5 to c. 30 nm. The single-layer tubes, on the other hand, all have extremely narrow diameters.

In the material produced by Bethune and colleagues, the tubes had diameters of 1.2 (±0.1) nm.

Following these initial studies, a great deal of work has now been carried out on optimizing the arc synthesis of single-walled tubes [22-28]. Helium at around 500–800 torr appears to be the most favourable atmosphere for SWNT production, and Fe, Co and Ni, or mixtures such as Ni/Y [23] are the most commonly used 'promoters' (we avoid the term 'catalysts' for these additives, as the process of nanotube formation is not catalytic). It has been shown that the addition of sulphur to the Co in the anode (either as elemental S, or as CoS), resulted in a much wider range of nanotube diameters than obtained from Co alone. Thus, single-walled nanotubes with diameters ranging from 1 to 6 nm were produced when sulphur was present in the cathode, compared to c. 1–2 nm for pure Co [24]. It was subsequently shown that bismuth and lead could similarly promote the formation of large-diameter tubes [25]. In 1997 a French group showed that high yields of single-walled nanotubes could be achieved with arc-evaporation [26]. Their method was similar to the original technique of Bethune and colleagues, but with a slightly different reactor geometry. Also, the promoter used was a Ni/Y mixture rather than the Co generally favoured by the Bethune group. The highest concentration of SWNTs was found to form in a 'collar' around the cathodic deposit, which made up approximately 20% of the total mass of evaporated material. Overall, the yield of tubes was estimated to be 70–90%. Examination of the 'collar' material by high-resolution electron microscopy showed many bundles of tubes, with diameters around 1.4 nm. In 2007, Marc Monthioux and colleagues showed that significantly improved yields could be achieved by using anodes made from either diamond powder or small grain graphite, rather than the usual large-grain graphite [28].

Although the iron group metals, with or without additives, are the most commonly used promoters, other metals including Rh, Pd and Pt [29,30] and rare earth metals [31-33] can also be used. When produced using rare earth metals, the tubes tend to be rather short, and are often found growing radially from the metal particles. An example, taken from the work of Saito and colleagues [32], is shown in Fig. 5. Unlike the iron group metals, the rare earth elements are not known as catalysts for the production of multiwalled nanotubes, so the formation of tubes on these elements is rather surprising, and the fact that the tubes grow on relatively large particles suggests that the mechanism may be different. It is worth noting that the radial growth of multiwall tubes from iron group metal particles was observed many years ago by Baker and others [34].

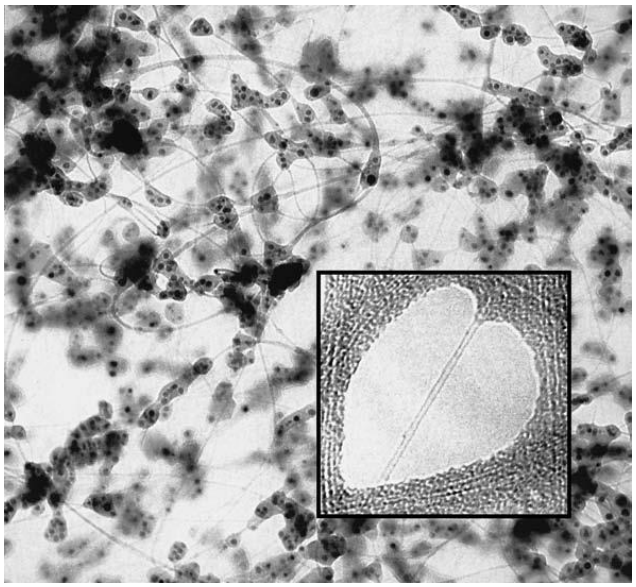

Fig 4: Images from the work of Bethune et al. [21] showing single-walled carbon nanotubes produced by co-vaporization of graphite and cobalt. The tubes have diameters of approximately 1.2 nm.

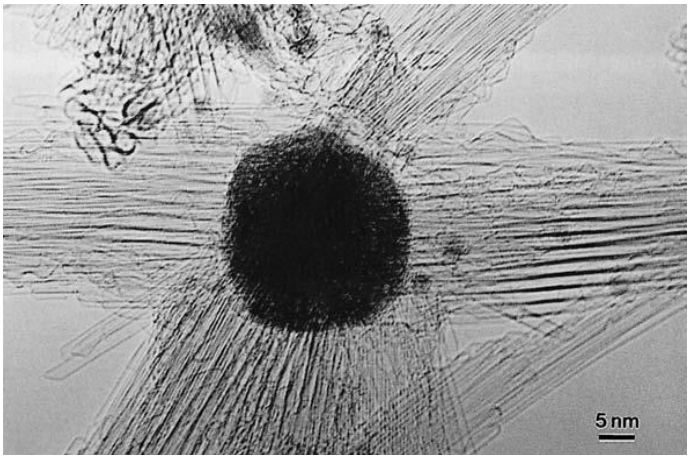

Fig 5: Single-layer nanotubes growing radially on a lanthanum particle [32].

2.2 Production of single-walled nanotubes by arc-evaporation:

C_{60} was first produced at Rice University in 1985 as a result of a programme of experiments on the vaporization of graphite using a Nd:YAG laser. In 1995 Smalley's group reported the laser vaporization synthesis of single-walled nanotubes [35]. Subsequent refinements of the method led to enhanced yields of single-walled tubes, which tended to form large bundles or 'ropes' [36]. The apparatus used by the Rice team illustrated schematically in Fig. 6. The furnace is heated to a temperature of approximately 1200 °C and an inert gas (typically argon) flows through the 5 cm diameter tube at a constant pressure of 500 torr. A cylindrical graphite target doped with small amounts of catalyst metal (typically 0.5–1.0% each of Co and Ni) is mounted at the centre of the furnace. Vaporization of the target is performed by a Nd: YAG laser. In the refined process [36], a double laser pulse was used to provide a more even vaporization of the target. This method was capable of producing up to 1 g per day of SWNTs, and the Rice group began selling samples commercially. The availability of these high-quality samples of SWNTs gave an important boost to nanotube research, and some important results were achieved using these samples. The laser vaporization method has been taken up by several other groups to make single-walled nanotubes, although the high cost of the powerful lasers required has perhaps prevented it becoming more widely used. In 1999 Iijima and colleagues produced SWNTs by irradiating a graphite–Co/Ni target with a 1 kW CO_2 laser [37]. It was found that nanotubes were produced even at room temperature, although the yield increased significantly when the oven temperature was increased to 1100–1200 °C. The effect of oven temperature on nanotube yield has been studied by a number of groups, as discussed in the next section. Several groups have explored the possibility of scaling up the laser vaporization process. In 2002, Peter Eklund of the Pennsylvania State University and colleagues used a 1 kW free electron laser at the Jefferson Lab in Virginia to produce SWNTs with production rates as high as 1.5 g h^{-1} [38]. It is interesting to note that Hongjie Dai's team have reported that the laser vaporization method appears to preferentially produce metallic SWNTs [39]. This potentially important finding does not seem to have been confirmed. Useful reviews of the production of single-walled nanotubes by laser vaporization have been given by Sivaram Arepalli [40] and by Christopher Kingston and Benoit Simard [41].

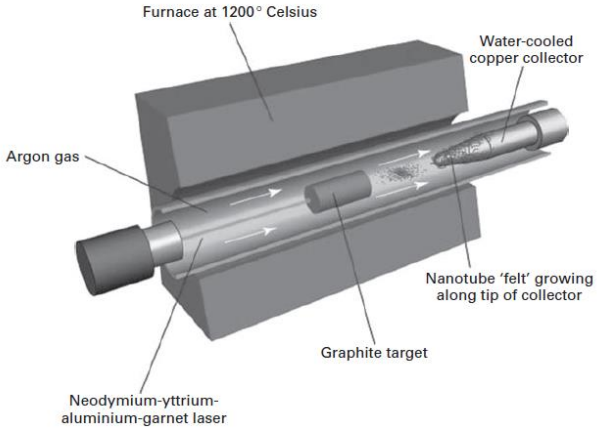

Fig 6: Oven laser-vaporization apparatus for the synthesis of single-walled carbon nanotubes [42].

2.3 Growth mechanisms of SWNTs in the arc and laser methods:

There are good reasons for assuming that the mechanisms of single-walled nanotube formation in the arc-evaporation and laser-vaporization processes are broadly similar. Both use similar starting materials, namely a graphite–metal mixture, and both involve the vaporization of this mixture followed by condensation in an inert atmosphere. Moreover, the nanotube-containing soot produced by both methods is identical in appearance, containing bundles of SWNTs together with disordered carbon and metal particles. Therefore,we assume that mechanisms proposed for one process are applicable to both. Although many different models have been mooted for the growth of SWNTs by the arc or laser methods, it is generally accepted that the mechanism probably involves 'root growth' rather than 'tip growth'. In other words, the tubes grow away from the metal particles, with carbon being continuously supplied to the base. This is supported by the fact that metal particles are not found at the tips of SWNTs produced by arc-evaporation or laser-vaporization, as would be the case if tip growth had occurred. Also, most of the particles observed in the SWNT-containing soot have diameters much larger than those of the individual tubes. The mechanisms which have been put forward for nanotube growth in the arc-evaporation and laser-vaporization methods will now be considered in detail.

2.3.1 Vapour–liquid–solid models:

Much the most popular mechanism for the growth of single-walled carbon nanotubes in the arc and laser methods is the vapour–liquid–solid (VLS) model. This kind of mechanism was first put forward in the early 1960s to describe the growth of whiskers of Si, Ge and other materials [43]. It was adapted by Tibbetts in 1984 [44] to explain the catalytic growth of multiwalled carbon nanotubes and was applied by Saito in 1995 to the growth of SWNTs in the arc [45]. The model assumes that the first stage of nanotube formation involves the co-condensation of carbon and metal atoms from the vapour phase to form a liquid metal carbide particle. When the particles are supersaturated, solid phase nanotubes begin to grow, as illustrated in Fig. 7. The driving force for the diffusion of carbon through the particles is either a temperature gradient or a concentration gradient. A number of detailed modelling studies, have been carried out based on the application of this mechanism to SWNT growth [46-50]. An illustration of the VLS growth of single-walled carbon nanotubes, from the work of Annick Loiseau and colleagues [48], is shown in Fig. 8. The first stage in this process is the formation of a liquid nanoparticle of metal supersaturated with carbon (Fig. 8a). On cooling, carbon begins to precipitate out of the solution, and can either form a graphitic coating on the particle surface (Fig. 8b) or can form seeds for the nucleation of single-walled nanotubes (Fig. 8c). Nanotube growth then proceeds through further incorporation of carbon atoms at the root (Fig. 8d). Figures 8(d) and (f) show situations where growth has been perturbed for some reason, resulting in the formation of short tubes and amorphous or graphitic C on the particle surfaces. Loiseau and co-workers used molecular dynamics simulations to model some of these processes. They firstly modelled the diffusion–segregation process occurring at the surface of the catalytic particle. The starting point was a cluster containing 51 Co atoms and 102 C atoms, which was first heated to 1727 °C, leading to random positions of Co and C within the cluster, and then cooled to 1227 °C, causing C atoms to segregate to the surface. The formation of a hexagon connected with two pentagons on the surface was observed, which the authors considered to be a possible first stage of the nucleation of a nanotube. A second simulation was then carried out which modelled the growth of a tube from an initial seed. This is illustrated in Fig. 9. The starting point was a small (6, 6) nanotube portion capped by a fullerene hemisphere, which was is placed on a slab of HCP Co, with 20 additional isolated carbon atoms on the particle surface. The system was then heated to 1227 °C, and diffusion of C atoms to the tube base, and incorporation into the nanotube structure, were observed.

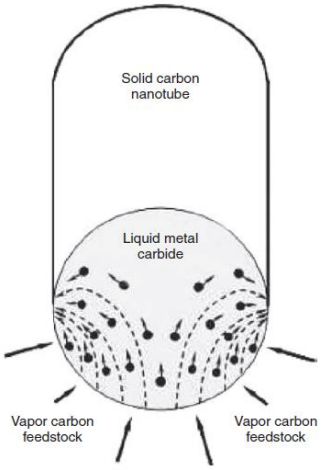

Fig 7: Illustration of the vapour–liquid–solid model for nanotube growth [46].

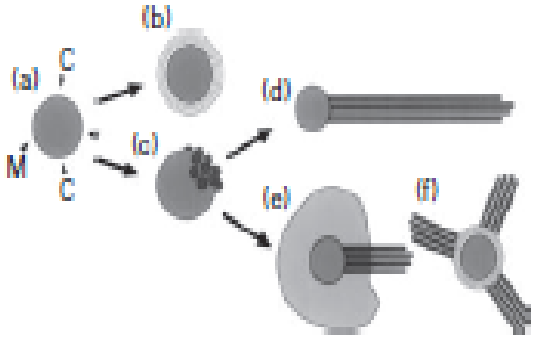

Fig 8: A scenario, based on the VLS mechanism, for nucleation and growth of SWNTs, from the work of Annick Loiseau and colleagues [48].

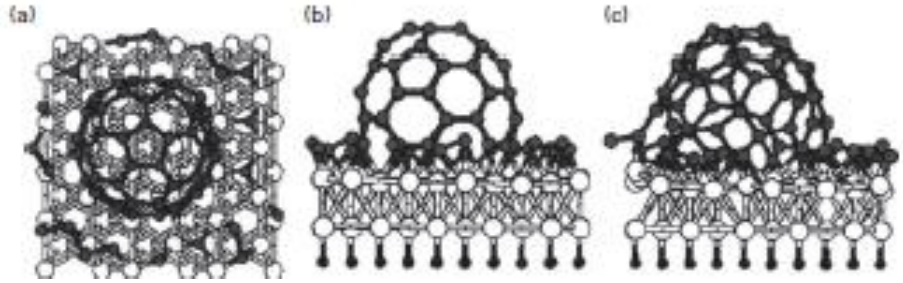

Fig 9: Simulation of the root growth mechanism for SWNTs extruded from large metal nanoparticles by Loiseau et al. [49].

Although Annick Loiseau and colleagues have modelled some of the key processes in the VLS growth of single-walled nanotubes, their treatment cannot be considered to be a complete simulation. The VLS model is also considered to be a plausible mechanism for the growth of SWNTs by CVD.

2.3.2 Solid-state models:

All the theoretical studies of SWNT formation discussed so far assume that the process involves a transformation of vapour phase carbon to solid carbon tubes, induced by the metal particles. Studies of SWNT production using the laser vaporization method published in 2001 and 2002 suggested that this model might not be correct, and that in fact the mechanism may involve a transformation of solid phase carbon [51-55]. The first of these studies was described by David Geohegan of Oak Ridge National Laboratory and colleagues in 2001 [51], whose work will now be summarized. This group had been studying the preparation of SWNTs by Nd:YAG laser vaporization of a graphite/Ni–Co target [52,53]. Their studies suggested that nanotube growth did not occur during the early stages of the process when carbon was in the vapour phase, but at a later stage when the 'feedstock' would be aggregated clusters and nanoparticles. In order to test the idea that SWNT growth is a solid-state transformation, they carried out further experiments involving the heat treatment of nanoparticulate soot containing short (~ 50 nm long) nanotube 'seeds'. This 'seeded' soot was produced by carrying out laser vaporization for shorter periods at a lower temperature than that used to produce full-length nanotubes. The soot collected from the laser vaporization apparatus was placed inside a graphite crucible under argon, and heated by a CO2 laser to temperatures up to 1600 °C. It was found that these heat treatments could produce micron length SWNTs, with optimum growth occurring at temperatures in the range 1000–1300 °C. Geohegan and colleagues put forward the following growth mechanism for SWNTs by laser vaporization. The Nd:YAG laser pulse initially produces an atomic-molecular vapour containing both carbon species and Ni/Co atoms. This evaporated material remains in the vapour phase for approximately 100 μs. The plasma then cools rapidly, and the carbon condenses and forms clusters ~200 μs after ablation (the metal atoms condense much later, at about 2 ms). The size of the carbon particles within the plume at these times does not exceed 20 nm at temperatures around 1100 °C. Geohegan et al. estimate the onset of SWNT growth to occur at 2 ms after ablation. By this time, both the carbon and the metal atoms are in a condensed form, so nanotube growth is largely a solid-state process. Studies similar to those of Geohegan and colleagues were carried out at about the same time by two other groups. Andre Gorbunov of Dresden University of Technology and co-workers prepared soot using laser vaporization, but at a temperature too low to induce nanotube formation [54] . This soot was then annealed at 1200 °C in an Ar atmosphere. This resulted in the formation of large numbers of single-walled nanotubes. On the basis of

this observation they put forward a growth model that involved the conversion of solid disordered carbon into nanotubes via liquid phase metal particles. The mechanism is clearly very similar to the vapour–liquid–solid model, but with a solid carbon source, and

was named the solid–liquid–solid (SLS) mechanism. The process is illustrated in Fig. 10. The first stage involves a molten catalyst nanoparticle penetrating a disordered carbon aggregate, dissolving it and precipitating carbon atoms at the opposite surface. These atoms then form a graphene sheet, whose orientation parallel to the supersaturated metal–carbon melt is not energetically favourable. Any local defect of this graphene sheet will therefore result in its buckling and the formation of a SWNT nucleus. The third study which independently demonstrated solid phase growth of singlewalled nanotubes was described by Hiromichi Kataura, then at Tokyo Metropolitan University, and colleagues [55]. Here, soot was obtained by laser ablation of Ni–Co– graphite composite targets at temperatures in the range 25–700 °C. The soot was then heated to 1200 °C in Ar. It was found that the soot which had been prepared using temperatures above about 550 °C yielded single-walled nanotubes after the 1200 °C treatment, but the soot prepared at lower temperatures did not. This is a very significant finding, for reasons we will return to below. On the basis of these observations, and of previous studies [56], Kataura and colleagues posited a model for SWNT growth, which is generally similar to the Geohegan mechanism, but which emphasizes the key role played by fullerene-like carbon fragments in nucleating growth. The model is illustrated in Fig.11. In the first phase, which occurs at a very early stage (μs) and at very high temperatures (2000–3000 °C), small carbon clusters nucleate. These have fullerene-like structures, rich in pentagonal rings. At this stage the metal atoms are still in the gas phase. As the system cools, metal atoms condense, forming particles or droplets, which become supersaturated with carbon, at around the eutectic temperature. The particles then become covered with fullerene-like carbon fragments. The ‘open edges’ of these fragments tend to stick to the particles to eliminate dangling bonds, and TEM observations suggest that in some cases the fragments form close-packed arrays. The fragments then act as precursors for SWNT growth, with carbon being supplied by precipitation from the particles or from the disordered carbon which surrounds the particles.

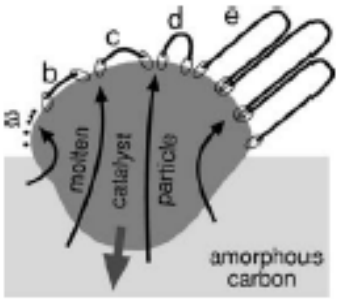

Fig 10: The solid–liquid–solid mechanism for the growth of single-walled carbon nanotubes from the work of Gorbunov et al. [54].

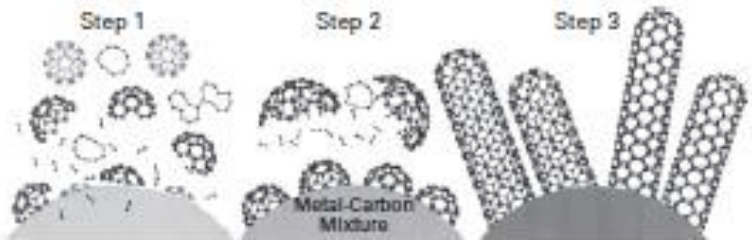

Fig 11: An illustration of a model for SWNT growth proposed by Kataura and colleagues [56].

3. CHEMICAL VAPOUR DEPOSITION

The catalytic chemical vapour deposition of carbon was reported already in 1959 [57], but only in 1993 carbon nanotubes were formed in this way [58]. During CVD, a substrate covered with metal catalysts, like nickel, cobalt, iron, or a combination is heated to approximately 700°C [59]. The growth starts after two gases are passed through the chamber, a carrier gas like nitrogen, hydrogen or argon, and some hydrocarbon gas like acetylene (C_2H_2) or methane (CH_4). The synthesis production yield, which indicates the amount of carbon nanotubes in the converted carbon, reaches 90%. CVD is commonly used for the industrial purposes because the method is already well investigated and offers acceptable results on the industrial-scale.

3.1 New Direction in the Chemical Vapour Deposition:

As for the fact that CVD is such a promising method for the production of carbon nanotubes, there is an ongoing research in this field. Some new methods were developed and some of them will be briefly presented in this chapter. CVD-method allows the pretreatment of the substrate surface which can lead to impressive, controlled multi-walled and single-walled nanotubes architectures [60]. Multi-walled nanotubes self-assemble into aligned structures because of the Van der Waals interaction between the single tubes. The substrates are catalytically patterned by the photolitography which enables selective deposition of the catalyst and consequently selective and controlled growth of carbon nanotubes. During CVD growth, the outer walls of the tubes interact with their neighbours via van der Waals forces, forming a rigid bundle which grows perpendicularly to the substrate [61,62]. In 2004 Sumio Iijima introduced another modification, the super-growth CVD or water-assisted CVD [63]. Here, the activity and lifetime of the catalyst are enhanced by addition of water into the CVD reactor. With this method dense, well-aligned "forests", perpendicular to the substrate with heights up to 2.5 mm can be produced [59]. With the low temperature CVD that was firstly reported in 2006 tungsten filament increases the decomposition of the precursor gases. Single-walled nanotubes were observed at temperatures as low as 350°C [63]. In 2007 a high-efficiency CVD-method based on hydrocarbon gas camphor ($C_{10}H_{16}O$) [64]was demonstrated. This technique promises to be especially environment-friendly.

4. CONCLUSION

This handout presented different production methods of carbon nanotubes Nowadays mostly used on industrial-scale techniques are chemical vapour deposition with its various modifications. Despite the huge volume of research on nanotube production since the publication of Iijima's paper in 1991, the arc-evaporation method remains the best method for the synthesis of high-quality multi walled tubes (for single-walled nanotubes the situation is rather different, as discussed below). The arc technique, however, suffers from a number of disadvantages. Firstly, it is labour intensive and requires some skill to achieve a satisfactory level of reproducibility. Secondly, the yield is rather low, since most of the evaporated carbon is deposited on the walls of the vessel rather than on the cathode, and the nanotubes are 'contaminated' with nanoparticles and other graphitic debris. Thirdly, it is a 'batch' rather than a continuous process, and it does not easily lend itself to scale-up. Turning now to single-walled nanotubes, it appears that the quality of the tubes is less dependent on the production method. Single-walled tubes produced by the arc and laser techniques are undoubtedly highly perfect, as shown by their excellent mechanical properties, but there is evidence that catalytically-produced SWNTs are equally perfect or more so. As far as growth mechanisms in the arc and laser methods are concerned, these remain obscure. In the case of multiwalled nanotubes, many different growth models have been put forward. For single-walled tubes produced by arc or laser vaporization, two types of growth model have been posited – the vapour–liquid–solid mechanism and the solid-state mechanism. Of these, the former is more widely accepted, and has been the subject of far more theoretical modelling. However, there appears to be experimental support for a solid-state mechanism, and some modelling studies of this type of growth would be of great value. The lack of understanding of the growth of both MWNTs and SWNTs by arc/laser vaporization is a serious impediment to progress in producing tubes with a defined structure or to developing methods for the mass production of high-quality tubes.

REFERENCES

[1] Iijima, S. Helical microtubules of graphitic carbon. Nature 1991, 354, 56–58.

[2] Radushkevich L.V.; Lukyanovich V.M. O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte. Zurn. Fisic. Chim. 1952, 26, 88–95.

[3] Oberlin, A.; Endo, M.; Koyama, T. Filamentous growth of carbon through benzene decomposition. J. Cryst. Growth 1976, 32, 335–349.

[4] Amelinckx, S.; Zhang, X.B.; Bernaerts, D.; Zhang, X.F.; Ivanov, V.; B.Nagy, J. A formation mechanism for catalytically grown helix-shaped graphite nanotubes. Science 1994, 265, 635–639.

[5] B.Nagy, J.; Bister, G.; Fonseca, A.; Méhn, D.; Kónya, Z.; Kiricsi, I.; Horváth, Z.E.; Biró, L.P. On the growth mechanism of single-walled carbon nanotubes by catalytic carbon vapor deposition on supported metal catalysts. J. Nanosci. Nanotech. 2004, 4, 326–345.

[6] Harris, P.J.F. Solid state growth mechanism for carbon nanotubes. Carbon 2007, 45, 229–239.

[7] Popov, V.N. Carbon nanotubes: Properties and application. Mat. Sci. Eng. R: Reports 2004, 43, 61–102.

[8] Paradise, M.; Goswami, T. Carbon nanotubes-production and industrial application. Mat. Design 2007, 28, 1477–1489.

[9] Grunlum, J.C.; Mehrabi, A.R.; Bannon, M.V.; Bahr, J.L. Water-based single-walled-nanotubefilled polymer composite with an exceptionally low percolation threshold. Adv. Mat. 2004, 16, 150–153.

[10] Supronowicz, P.R.; Ajayan, P.M.; Ullman, K.R.; Arulanandam, B.P.; Metzger, D.W.; Bizios, R. Novel current-conducting composite substrates for exposing osteoblast to alternating current stimulation. J. Biomed. Mat. Res. A 2002, 59, 499–506.

[11] Koerner, H.; Price, G.; Pearce, N.A.; Alexander, M.; Varia, R.A. Remotely actuated polymer nanocomposite-stress-recovery of carbon nanotube filled thermoplastic elastomers. Nature Mater. 2004, 3, 115–120.

[12] Sen, R.; Zhao, B.; Perea, D.; Itkis, M.E.; Hu, H.; Love, J.; Bekyarova, E.; Haddon, R.C. Preparation of single-walled carbon nanotube reinforced polystyrene and polyurethane nanofibers and membranes by electrospinning.

[13] .NanoLett. 2004, 4, 459–464. 13 Lin, Y.; Taylor, S.; Li, H.; Fernando, S.K.A.; Qu, L.; Wang, W.; Gu, L.; Zhou, B.; Sun, Y.P. Advances toward bioapplications of carbon nanotubes. J. Mater. Chem. 2004, 14, 527–541.

[14] J.A.Isaacs, A.Tanwani, M.L.Healy, L.J.Dahlben; J Nanopart Res, 12:551-562 (2010).

[15] T.Guo, P.Nikolaev, A.Thess, D.T.Colbert, R.E.Smalley; Chem.Phys.Let. 243(1,2), 49-54 (1995)

[16] C.Journet, W.K.Maser, P.Bernier, A.Loiseau et al; Nature 388, 756-758 (1997).

[17] R. S. Ruoff; J. Tersoff; D. C Lorents; S. Subramoney, B. Chan (1993). "Radial deformation of carbon nanotubes by van der Waals forces". Nature. 364 (6437): 514–516.

[18] M. Tomita, Y. Saito and T. Hayashi, 'LaC2 encapsulated in graphite nanoparticle', Jap. J. Appl. Phys., 32, L280 (1993).

[19] S. Seraphin, D. Zhou, J. Jiao et al., 'Yttrium carbide in nanotubes', Nature, 362, 503 (1993).

[20] D. S. Bethune, C. H. Kiang, M. S. de Vries et al., 'Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls', Nature, 363, 605 (1993).

[21] S. Iijima and T. Ichihashi, 'Single-shell carbon nanotubes of 1-nm diameter', Nature, 363, 603 (1993).

[22] B. Hornbostel, M. Haluska, J. Cech et al., Carbon Nanotubes, Proceedings of the NATO Advanced Study Institute, ed. V. N. Popov and P. Lambin, Springer-Verlag, Berlin, 2006, p. 1.

[23] M. E. Itkis, D. E. Perea, S. Niyogi et al., 'Optimization of the Ni–Y catalyst composition in bulk electric arc synthesis of single-walled carbon nanotubes by use of near-infrared spectroscopy', J. Phys. Chem. B, 108, 12 770 (2004). 40 Synthesis I: arc- and laser-vaporization, and heat treatment methods.

[24] C. H. Kiang, W. A. Goddard III, R. Beyers et al., 'Carbon nanotubes with single-layer walls', Carbon, 33, 903 (1995).

[25] C. H. Kiang, P. H. M. van Loosdrecht, R. Beyers et al., 'Novel structures from arc-vaporized carbon and metals: single-layer nanotubes and metallofullerenes', Surf. Rev. Lett., 3, 765 (1996).

[26] C. Journet, W. K. Maser, P. Bernier et al., 'Large-scale production of single-walled nanotube nanotubes by the electric-arc technique', Nature, 388, 756 (1997).

[27] M. Takizawa, S. Bandow, M. Yudasaka et al., 'Change of tube diameter distribution of single-wall carbon nanotubes induced by changing the bimetallic ratio of Ni and Y catalysts', Chem. Phys. Lett., 326, 351 (2000).

[28] A. Mansour, M. Razafinimanana, M. Monthioux et al., 'A significant improvement of both yield and purity during SWCNT synthesis via the electric arc process', Carbon, 45, 1651 (2007).

[29] Y. Saito, K. Nishikubo, K. Kawabata et al., 'Carbon nanocapsules and single-layered nanotubes produced with platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt) by arc discharge', J. Appl. Phys., 80, 3062 (1996).

[30] Z. H. Li, M. Wang and Y. Saito, 'Effect of Rh and Pt on growth and structure of single-walled carbon nanotubes', Inorg. Mater., 42, 605 (2006).

[31] S. Subramoney, R. S. Ruoff, D. C. Lorents et al., 'Radial single-layer nanotubes', Nature, 366, 637 (1993).

[32] Y. Saito, M. Okuda, M. Tomita et al., 'Extrusion of single-wall carbon nanotubes via formation of small particles condensed near an arc evaporation source', Chem. Phys. Lett., 236, 419 (1995).

[33] D. Zhou, S. Seraphin and S. Wang, 'Single-walled carbon nanotubes growing radially from YC2 particles', Appl. Phys. Lett., 65, 1593 (1994).

[34] R. T. K. Baker and R. J. Waite, 'Formation of carbonaceous deposits from catalysed decomposition of acetylene', J. Catalysis.

[35] T. Guo, P. Nikolaev, A. Thess et al., 'Catalytic growth of single-walled nanotubes by laser vaporization', Chem. Phys. Lett., 243, 49 (1995).

[36] A. Thess, R. Lee, P. Nikolaev et al., 'Crystalline ropes of metallic carbon nanotubes', Science, 273, 483 (1996).

[37] F. Kokai, K. Takahashi, M. Yudasaka et al., 'Growth dynamics of single-wall carbon nanotubes synthesized by CO2 laser vaporization', J. Phys. Chem. B, 103, 4346 (1999).

[38] P. C. Eklund, B. K. Pradhan, U. J. Kim et al., 'Large-scale production of single-walled carbon nanotubes using ultrafast pulses from a free electron laser', Nano Lett., 2, 561 (2002).

[39] Y. M. Li, D. Mann, M. Rolandi et al., 'Preferential growth of semi-conducting single-walled carbon nanotubes by a plasma enhanced CVD method', Nano Lett., 4, 317 (2004).

[40] S. Arepalli, 'Laser ablation process for single-walled carbon nanotube production', J. Nanosci. Nanotech., 4, 317 (2004).

[41] C. T. Kingston and B. Simard, 'Recent advances in laser synthesis of single-walled carbon nanotubes', J. Nanosci. Nanotech., 6, 1225 (2006).

[42] B. I. Yakobson and R. E. Smalley, 'Fullerene nanotubes: C1,000,000 and beyond', Amer. Sci., 85, 324 (1997).

[43] R. S. Wagner and W. C. Ellis, 'Vapor-liquid-solid mechanism of single crystal growth', Appl. Phys. Lett., 4, 89 (1964). References 41

[44] G. G. Tibbetts, 'Why are carbon filaments tubular?', J. Cryst. Growth, 66, 632 (1984).

[45] Y. Saito, 'Nanoparticles and filled nanocapsules', Carbon, 33, 979 (1995).

[46] K. Bolton, F. Ding and A. Rosén, 'Atomistic simulations of catalyzed carbon nanotube growth', J. Nanosci. Nanotech., 6, 1211 (2006).

[47] Y. Shibuta and S. Maruyama, 'Molecular dynamics simulation of generation process of SWNTs', Physica B, 323, 187 (2002).

[48] J. Gavillet, A. Loiseau, C. Journet et al., 'Root-growth mechanism for single-wall carbon nanotubes', Phys. Rev. Lett., 87, 275504 (2001).

[49] J. Gavillet, A. Loiseau, F. Ducastelle et al., 'Microscopic mechanisms for the catalyst assisted growth of single-wall carbon nanotubes', Carbon, 40, 1649 (2002).

[50] C. L. Luo, H. W. Yu, Y. Q. Zhang et al., 'Simulations of nucleation of single-walled carbon nanotubes', Physica Status Solidi A, 204, 555 (2007).

[51] D. B. Geohegan, H. Schittenhelm, X. Fan et al., 'Condensed phase growth of single-wall carbon nanotubes from laser annealed nanoparticulates', Appl. Phys. Lett., 78, 3307 (2001).

[52] A. A. Puretzky, D. B. Geohegan, X. Fan et al., 'In situ imaging and spectroscopy of single-wall carbon nanotube synthesis by laser vaporization', Appl. Phys. Lett., 76, 182 (2000).

[53] A. A. Puretzky, H. Schittenhelm, X. Fan et al., 'Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization', Phys. Rev. B, 65, 245425 (2002).

[54] A. Gorbunov, O. Jost, W. Pompe et al., 'Solid–liquid-solid growth mechanism of single-wall carbon nanotubes', Carbon, 40, 113 (2002).

[55] R. Sen, S. Suzuki, H. Kataura et al., 'Growth of single-walled carbon nanotubes from the condensed phase', Chem. Phys. Lett., 349, 383 (2001).

[56] H. Kataura, Y. Kumazawa, Y. Maniwa et al., 'Diameter control of single-walled carbon nanotubes', Carbon, 38, 1691 (2000).

[57] P.L.Walker Jr, J.F.Rakszawski, G.R.Imperial; J. Phys. Chem. 63 2 133 (1959)

[58] M.José-Yacamán, M.Miki-Yoshida, L.Rendón, J.G.Santiesteban; Appl.Phys.Let. 62 (6): 657 (1993).

[59] http://en.wikipedia.org/wiki/Carbon_nanotube.

[60] W.Z.Li, S.S.Xie, L.X.Qian, B.H.Chang, B.S.Zou, W.Y.Zhou, R.A.Zhao, G.Wang; Science 274, 1701-1703 (1996).

[61] H. Dai, Phys. World (2000).

[62] J.Li, C.Papadopoulos, J.M.Xu; Appl.Phys.Let.75-3-19.07 (1999).

[63] K.Hata et al; Science 306 (5700): 1362-1365 (2004).

[64] Cantoro, Hoffman, Pisana, Robertson; Nano Letters, Vol6,No6,1107-1112 (2006).