Methods of Carbon Nanotube Production

Carbon Nanotubes (CNTs) have shown the potential to change the engineering world with their unprecedented strength, stiffness and semiconductive capabilities. However, the production and alignment of masses of high quality nanotubes has proven challenging at an industrial scale. This paper assesses the effectiveness of the three leading methods of CNT production in terms of quality, yield, cost and scalability. Chemical Vapour Deposition was found to produce higher quality CNTs at greater yields and lower costs than Arc-discharge or Laser Ablation. By engaging catalysts at the gas stage of production and utilising well-developed technology, it also has shown the most potential for large-scale implementation.

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Introduction

Carbon Nanotubes (CNTs) are composed of one-atom thick layers of graphene rolled into cylinders with a diameter of nanometric order. These seamless cylinders have multiple interesting properties due to the variety of potential sizes and geometries they can possess [1]. Individual CNTs have been shown to possess a tensile strength 100 times greater than steel and an axial stiffness almost ten times greater than carbon fibre [2, 3]. Once produced, the tubes can be woven into continuous fibres of immense strength with numerous potential applications in structural and mechanical engineering. In addition, their adaptable, helical nature gives CNTs the ability to act both metallically and semi-conductively. This could allow semiconductors to be manufactured smaller and simpler than current silicon semiconductors, which additionally require chemical doping [4]. As semiconductors are the foundation of modern electronic devices, this would have a significant impact on electrical, biomedical and multiple other fields of engineering.

As of yet, carbon nanotube production has yet to be fully developed and no industry-wide process currently exists. However, several papers have been published on the topic of the continuous production of CNTs and research is currently being conducted. Notably, A. J. Hart, associate professor at MIT, has published multiple studies on how to implement large-scale production, including the use of standard laser printers [5-7]. In this paper, I shall be assessing the three leading methods of CNT production and evaluating their yield quality, yield quantity, cost and energy efficiency, and potential for large-scale application. Currently, the most effective technique for creating high quality carbon nanotubes is Chemical Vapour Deposition, in preference to Arc-discharge or Laser Ablation.

Background

Since the creation of the first carbon nanotubes in 1976, significant difficulties concerning CNT production have been encountered [8]. Firstly, CNTs need to be arranged into regular patterns in order to be woven in fibres that can be utilised effectively. This is either very difficult or impossible for many production methods. In addition, the diameter of the tubes should be minimised to maximise strength, and the tube length maximised to increase efficiency [9]. Figure 1 illustrates the inverse proportionality of CNT diameter and collapse pressure. However, our ability to manipulate the size of CNTs is limited and differs greatly between methods. Furthermore, the electrical conductivity of CNTs is determined by the helical geometry, or chirality, of the tube structure [10]. Controlling this geometry is a task of even greater difficulty.

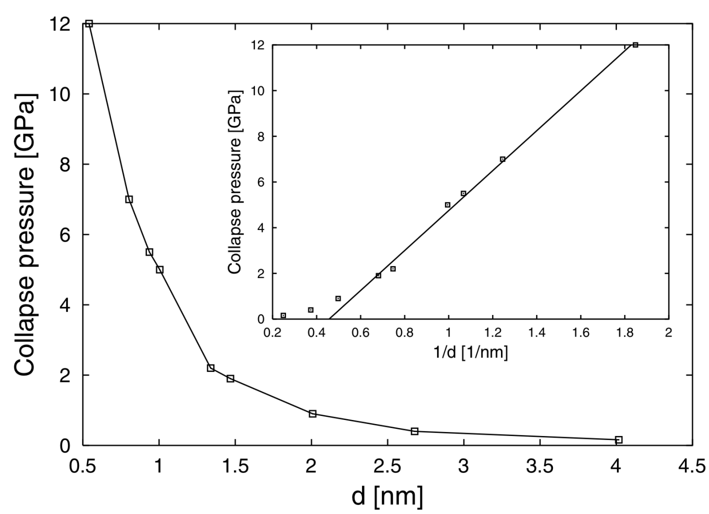

Figure 1. Collapse pressure of carbon along axial dimension as a function of tube diameter, and (inset) as a function of reciprocal diameter [9].

All of the aforementioned issues concern the quality of the carbon nanotubes. However, there are considerably more problems that require addressing. Firstly, the quantity of carbon nanotubes produced must be great enough for the process to be economically feasible. Secondly, the procedure must be ecologically sustainable in order for a significant amount of CNTs to be grown. Finally, for CNTs to have a lasting impact on the world, the production method must have potential for large-scale, industrial application. This requires minimising the equipment size, the need for human maintenance and any post-manufacturing operations such as separation or purification.

One method of CNT production is Arc-discharge. First discovered in 1991 by Iijima while working at NEC, it involves the generation of an arc of electricity at 4000°C between two carbon electrodes in a large, metal reactor [11, 12]. This reactor, as shown in Figure 2, contains an inert gas atmosphere that must be maintained at a constant high pressure. Carbon soot gathers on the negative electrode, which most frequently contains a catalyst of Nickel or Cobalt origin, from which the nanotubes are gathered. The nanotubes he created had very small diameters of around 1nm and the yield efficiency was consistently between 70% and 90% [11, 13]. However, some authors have only been able to recreate efficiencies of 10% to 50% [14]. In addition, the actual yield quantity is significantly limited by the small size of the graphite electrodes used. Furthermore, producing the arcs of electricity that are required is relatively energy intensive [15].

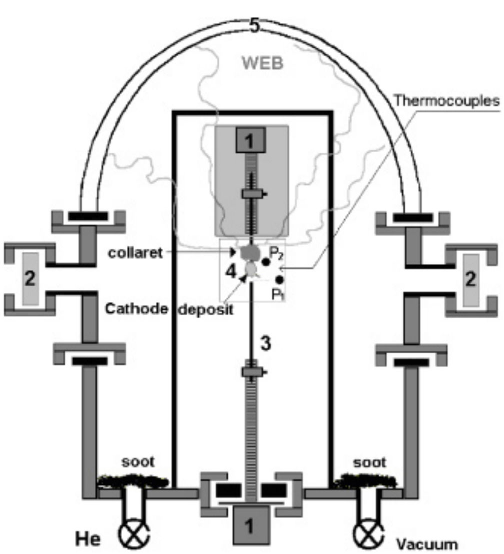

Figure 2. Arc-discharge apparatus.
Source: iopscience.iop.org.

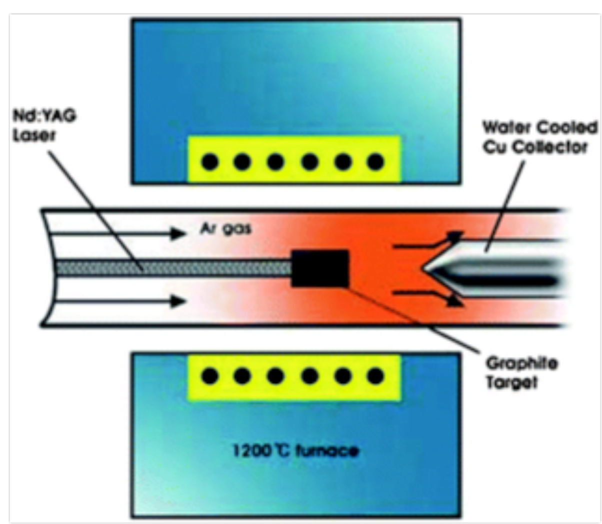

Figure 3. Laser Ablation apparatus.
Source: kazuli.com/nanotubes

An additional method of producing CNTs is Laser Ablation. In this method, a laser is fired at a large graphite target in the presence of an inert gas. The graphite is vaporised and carbon nanotubes condense on the surfaces of the reactor, as shown in Figure 3 [12]. The diameters of the nanotubes grown vary between studies but Smalley et al. achieved the consistent production of CNTs of diameter 1.4nm ±0.2 [16]. Yield percentage has been found to be between 50% and 80% [4, 16, 17]. However, similarly to Arc-discharge, the yield quantity is limited by the size of the graphite targets [18]. In addition, high yield results have only occurred where the process has been successfully raised to 1200°C. By altering the catalysts involved in the reaction, Smalley et al. also found that the size of the CNTs could be manipulated.

Currently, the most common method of CNT production is Chemical Vapour Deposition (CVD). This procedure involves the reaction of hydrocarbon gases at 700-900°C at atmospheric pressure. CNTs form from the deposition of these gases onto a metal substrate [19]. Multiple studies using various CVD methods have produced nanotubes with diameters consistently as small as 0.7nm [20, 21]. In addition, yield efficiency has been measured between 70% and 80% [21, 22]. Most importantly however, the CVD method can be aided by the use of plasma beds to align the growth of CNTs [23]. This method also allows us to determine the approximate diameter, length and chirality of the tubes pre-production. Certain variations of CVD, such as the HiPco process, introduce the catalyst at the gas stage rather than post-reaction. This means that the nanotube growth stage is not under catalytic support and the reaction can run continuously without maintenance [21, 24]. All CVD reactions are conducted at temperatures of 700-1100°C [19].

Discussion

Regarding the quality of the carbon nanotubes produced, all three methods are capable of consistently growing CNTs of around 1nm in diameter. However, CVD has produced the smallest diameter nanotubes at 0.7nm. CVD and Laser Ablation have produced the longest specimens of CNTs, however, the CVD method gives us the greatest control over the size and length of the nanotubes to be grown. In addition, the CVD method gives us control of CNT alignment and chirality. In contrast, CNTs produced by Arc-discharge or Laser Ablation form in tangled piles that also contain other unwanted carbon molecules and catalyst residue.

At optimum conditions, all three methods have recorded similar efficiencies of around 70% to 80%. However, the quantity grown via the Arc-discharge method is severely limited by the small amount of initial carbon in the electrodes. A similar issue is faced with Laser Ablation, as the graphite targets used limit the source of carbon and are difficult to manufacture. In comparison, the hydrocarbon gases used in the CVD process are abundant and easy to handle. As a result, the real yield quantity of the CVD method is far higher than that of Arc-discharge or Laser Ablation.

Cost and energy efficiency vary greatly between CNT production methods. Arc-discharge is an expensive process, as it requires large and expensive custom apparatus to be built. The energy needed to produce the electric arcs at 4000°C is also considerable. Furthermore, the whole reaction environment needs to be kept at a very high pressure in the presence of an inert gas, which adds a significant amount to the already high cost. Laser Ablation suffers from analogous problems. The necessary lasers are high power and draw large amounts of energy, and the entire process requires a constant reaction temperature of 1200°C and a high pressure, inert environment. The graphite targets that are consumed are also expensive to produce. In contrast, CVD has no active, high-energy processes like Arc-discharge or Laser Ablation. Furthermore, the reactions occur at only 700-900°C at standard atmospheric pressure.

Large-scale, industrial production is crucial for the development of carbon nanotubes. The potential for the continuous application of Arc-discharge and Laser Ablation is severely limited by the large initial requirements and running costs. The constant replacement of graphite targets and catalyst beds would also require considerable human input and slow down production rates. The process of vapour deposition that the CVD method utilises has existed since the 1960s [25]. Therefore, the equipment needed is well developed and easily attainable. In addition, running costs are small due to the abundance of raw materials, low running temperature and standard atmospheric environment. Furthermore, CVD is the only method where catalyst introduction at the gas phase is possible. This allows the growth of the CNTs to occur continuously without catalytic support. This makes the process ideal for industrial-scale operation, as it requires very little human input and very low input requirements.

Conclusion

Overall, Chemical Vapour Deposition shows the most potential as an effective, large-scale method of CNT production. This is due to its capacity to produce nanotubes of size, length and chirality that we can control. Control over the tube geometry allows us to utilise the semiconducting nature of the CNTs and has the potential to revolutionise modern day electronics. In addition, CVD is the only method that can produce vertically aligned CNTs that can be woven into fibres. This is a prerequisite for any structural or weight-bearing application of CNTs, an area of huge development capacity. CVD is also the most cost effective and energy efficient method of the three assessed. The technology and raw materials already exist in abundance. Furthermore, it requires the least human input during the reaction process. This makes it the ideal method for industrial operations.

Recommendations

I suggest that Chemical Vapour Deposition be utilised as a large-scale method for the production of vertically aligned carbon nanotubes. Plasma beds should be used to align the CNTs into pre-determined patterns to maximise structural applications and pre-production catalysts should be applied to maximise yield. Efforts should be made into creating a fibre-based reinforced polymer, similar to that of standard carbon fibre polymers. This will allow carbon nanotube technology to transform the engineering world by giving engineers access to stronger and stiffer materials at a reduced weight. Finally, the semiconducting properties of CNTs should be further investigated via the manipulation of the CVD method, as CNTs have the potential to take a significant role in the future of electronics.

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