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Review

An overview on methods for the production of carbon nanotubes

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ABSTRACT

Carbon nanotubes (CNTs) are one of the most exciting discoveries in nanoscale sciences. A brief survey of experimental work directed towards the synthesis of CNTs has been discussed. The various methods of production of CNTs are explained outlining their capabilities, efficiencies and possible exploitation as economic large scale production. Among the discussed techniques, the chemical vapor deposition (CVD) appears to be the most potential way to produce high quality of CNTs at high yield. The advantages of CVD over other techniques are also explained and the effects of process parameter on the synthesis of these nanomaterials are discussed.

Contents

1. Introduction

Nowadays, many researches [1–4] concentrate on the field of carbon. The most popular is the identification of the structure of the fullerenes in 1985 by Kroto et al. [1]. A further study in 1991 by Iijima [2] discovered the multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs), whereas the SWCNTs were independently discovered by Iijima and Ichihashi [3] and Bethune et al. [4]. Earlier to the discovery of nanotubes, the significance of the investigations made on carbon fibres with diameters bigger than 7 nm was not clear until the connection between fullerenes and nanotubes was revealed. One of the articles [5] that reported about the decade of discovery of nanotubes, it is e.g. stated that nanotubes were unintentionally produced by chemists experimenting on methane in the late nineteenth century [6]. In 1960, nanoscale scrolls of graphite were produced by Bacon [7]. The truth is that Iijima who has generated a mixture of scrolls and tubes by using his own procedure [8–10], suggests that Bacon may have also done this. In 1976 Oberlin et al. [11] clearly showed a hollow carbon fibre with nanometer-scale diameters using a vapor-growth technique. Wiles and Abrahamson [12] in 1979, found "mats of small fibres" on one electrode when sparks were passed between two graphite electrodes. Gibson [13] reported that, Davis et al. [14] were the first to see a nanotube, but some researchers like Monthioux and Kuznetso [15] in 2006,

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agreed that the credit should be given to Radushkevich and Lukyanovich [16] in 1952 for producing first nanometric-sized carbon filaments.

The researchers [17] who investigated on the growth of vapor grown carbon fibres may have also yielded nanotubes because the technique used nowadays to produce nanotube is similar. Due to the extraordinary mechanical [18,19], thermal [20] and electronic and magnetic [21,22] properties, the CNTs become a favorable area to be studied for its various potential applications. The CNTs have been adopted in several applications such as in electron-field emitters in panel displays [23,24], single-molecular transistors [25], scanning probe microscope tips [26,27], gas [28] and electrochemical energy storage [29], hydrogen storage [28,30] catalyst supports [31], molecular-filtration membranes [32], polymer fillers [33], strain sensors [34], chemical sensors [35] high-power capacitors [36], quantum resistors [37], long ballistic conductors [38], nanotweezers [39], nanoelectronic devices [40], artificial muscles [41] and the next generation of molecular electronic devices [42]. Various methods to grow the CNTs have been developed, including laser ablation [43], arc discharge [44] and chemical vapor deposition (CVD) [45].

In this study, the methods to produce CNTs will be explained and the comparisons between these techniques are highlighted. CVD becomes the area of interest due to its potential in producing high quality and high yield of CNTs particularly in industrial applications. Furthermore, the effect of process parameters to synthesis CNTs will be discussed.

2. Production of carbon nanotubes

Generally, there are few techniques employed to produce CNTs such as electric- arc discharge, laser ablation and CVD. By using any of these techniques, different type of CNTs, can be produced such as vapor grown, carbon fiber and types of carbon nanostructure materials.

2.1. Electric-arc discharge

Electric-arc discharge is known to be the most common technique and also one of the oldest ways in the CNTs production. This method is known to be a traditional and simple device to produce high temperature needed to evaporate carbon atoms in plasma. Iijima [2] was the one who first observed the CNTs structure using this method. By using this method, the electric arc vaporizes a hollow graphite anode packed with a mixture of transition metals (such as Fe, Co or Ni) and graphite powder. The inert gas flow is maintained at 50–600 Torr. Nominal conditions involve 2,000–3,000 °C, 100 amps and 20 V (Iijima [2], Ebbesen and Ajayan [46], Ching-Hwa et al. [47], Journet and Bernier [43] and Jung et al. [48]). The variation of process parameters such as flow rate, gas pressure, and metal concentration is needed to obtain the highest yield of CNTs which occurred in 'pillar-like tubes' either in single- walled tubes or multi- walled tubes. The structures of the nanotubes produced are usually short tubes. SWCNTs with diameters ranging from 0.6 to 1.4 nm and 10 nm diameter MWCNTs, this method is relatively easy to be implemented and 30% yield will be obtained. The content of impurities in CNTs produced is higher compared to other methods, and the consistency of the shape, wall, and lengths of the tubes are somewhat random [43].

Two carbon electrodes are used in the carbon arc discharge technique to produce an arc by digital current (DC). Fig. 1 shows schematic of arc-discharge to produce CNTs. Initially, the two electrodes are kept independent. The electrodes are kept in a vacuum chamber and an inert gas is supplied to the chamber. The inert gas increases the speed of carbon deposition. Once the pressure is stabilized, the power supply is turned on (about 20 V). The positive electrode is then gradually brought closer to the negative one to strike the electric arc. The electrodes become red hot and a plasma forms. Once the arc stabilizes, the rods are kept about a millimeter apart while the CNT deposits on the negative electrode. Once the specific length is reached, the power supply is cut off and the machine is left for cooling. Precaution needed for the important parameters are; (1) the control of arcing current and (2) the optimal selection of inert gas pressure in the chamber [49,50].

The CNTs are usually produced by striking an arc between graphite electrodes a atmosphere (He or Ar), this method also produces carbon soot materials which contain fullerence molecules (Iijima 1991). The carbon arc provides a suitable instrument to create high temperatures required to vaporize carbon atoms into a plasma (>3,000 °C) (Ebbesen et al. [51] and Seraphin et al. [52]) normally the yield and purity of CNTs are based on the sensitivity of gas pressure vessel occurred between the electrodes, current density, inert gas pressure and stability. A very high ionization potential [53] makes gasses such as He atmosphere gives good results, perhaps due to its very high ionization potential (Ebbesen et al. [53]) However, some works [54] also reported the use of methane or hydrogen atmosphere. The well-cooled electrodes and arc chamber will be useful in maximizing the yield of CNTs.

For the MWCNT production, the conditions are optimized during arc discharge utilizing the DC current between two graphite; usually for water-cooled electrodes with diameters between 6 and 12 mm in a chamber filled with He sub atmospheric pressure, the soot produced is minimized and 75% of evaporated carbon is made to deposit onto the opposite graphite cathode surface from graphite anode. The deposited pyrolytic was removed from the cathode that consists of 3 to 4 layers having 0.3 to 0.4 cm thickness that needs to be grind for the carbon deposit on morphology and yield of product. The grinding of the sample was carried out in three ways, the mortar and pestle, ball milling with alumina balls and tungsten carbide grid. Depending upon the nature of grinding the sample, the morphology of the sample is quite different from each. The optimal conditions were at 20–25 V, 50–100 Amp. The DC, current density 90 A/Cm^2 and the He pressure maintained at 500 Torr. This method is a variant and easy process to produce high quality of CNTs having 15 to 60 nm in diameter. However, this technique is not a regular and unstable method and the yield of CNTs is very less. From these methods, the amount of CNT on the cathode surface and electrode gap is not constant, as the results, the current flow is not uniform throughout and electric filed are non-homogenous. The temperature distribution and density of carbon vapor is not uniform and the impurities present on the surface of CNT collected are not constant, the consequence current flow is not uniform throughout and electric filed are non-homogenous. Hence, the temperature distribution and density of carbon vapor are not uniform and impurities were present on the surface of CNTs. To solve these problems that occur during the synthesis of CNTs, many researchers (Gamaly and Ebbesen [54], Byszewski et al. [55]) have conducted the studies to understand the mechanism of nanotube to produce large scale synthesis of MWCNTs using these techniques [46].

Lee et al. [56] used the plasma rotating arc discharge to produce large amount of CNTs where high velocity has been adopted to rotate the graphite anode for the synthesis of CNTs. The stable plasma was generated by the rotation of the anode with the distribution of the microdischarges homogeneously. The acceleration of the carbon vapor perpendicular to the anode is generated by the rotation of the centrifugal force. It is not condensed at the cathode surface but collected on the graphite collector that was placed at the periphery of the plasma. The nanotube yield increases as the rotation speed of the anode increases and the collector