A Brief Description of Carbon Nanotubes: History, Synthesis, and Properties: A Study

Dr Shailendra Kumar Srivastava Associate Professor Department of Physics MGPG College Gorakhpur Dr Subhash Kumar Sharma Assistant Professor Department of Physics MGPG College Gorakhpur

Abstract

Carbon nanotube (CNT) is one of the most widely used nano materials recently. Since it was discovered by Iijima in 1991, its various synthesis methods were being mature in the past 30 years. The research of carbon nanotube applications in different fields has never stopped. Since a number of researchers have tested the excellent properties of CNTs, it provides an optimistic expectation about CNT applications in the future. This review summarizes the historical development of CNTs, and briefly introduces three main CNT synthesis methods and their properties.

Keywords: Carbon Nanotubes ,Nano materials

Introduction

Carbon Nanotube (CNT) is single-layer graphene rolled into a tube. The single-wall Carbon Nanotube (SWCNT) was discovered in 1991, by Iijima and Ichihashi. They reported the growth of 1-nm SWCNT by the carbon-arc synthesis [1, 2]. Just like fullerene and graphene, SWCNTs are one of the allotropes of carbon. The consisting of nested SWCNTs refers to the multi-wall carbon nanotubes (MWCNTs), bounding together weakly by van der Waals interactions. The bonds between carbon atoms provide CNT not only exceptional tensile strength, but also excellent thermal conductivity [3-5]. CNT has many other fascinating properties such as electrical conductivity that were examined in subsequent research. The diameter of CNTs usually measured in nano meters, so it is one of the widely applicated nano materials due to its various physicochemical properties, such as field emission devices, hydrogen storage media, and nano sensors.

History

Carbon Nanotube (CNT) was firstly discovered in 1991, and then it reported by Iijima and Ichihashi reported the single-wall carbon nanotube synthesis with diameter of 1 nano meter in 1993 [1], [2]. Carbon nanotube (CNT) also known as Bucky tube is a class of nano materials composed, which is of two-dimensional hexagonal lattice of carbon atoms. They are bent in one direction, and also combined to form a hollow cylindrical cylinder. Carbon nanotubes are allotropes of carbon, which are described between Fullerene (0 dimensional) and Graphene (2 dimensional). Most research and applications of carbon nanotubes have focused on tubes that range in circumference from a few graphene cells to hundreds of cells. Half of a meter long carbon nanotube has been produced, with aspect ratios in excess 100000000:1. Depends on the desire, the length of carbon nanotubes can be assumed to be infinitely long [6]. According to the different structure of carbon nanotubes, there are two kinds; one is multi-walled carbon nanotubes (MWCNTs), the other is single-walled carbon nanotubes (SWCNTs). Single-walled carbon nanotubes are one layer of graphite, while multi-walled nanotubes are multilayer concentric graphite [2]. This article we will give a brief introduction about CNT, including its development history, recent applications, synthesis methods, and properties.

History of Carbon Nanotubes

The true identity of the discoverers of carbon nanotubes is a subject of debate. The mainstream scientific community believes that Lijima from Japanese electric co.,LTD.(NEC) found the CNT. In 1991, Lijima published a paper expounds his discovery, the discovery caused a frenzy and inspired many scientists are studying the application of carbon nanotubes [2]. Although Lijima is credited with discovering carbon nanotubes, it turns out that the timeline for carbon nanotubes dates back well before 1991. In 1952, Radushkevich and Lukyanovich, two brilliant researcher, who published a sharp image of 50 carbon nanotubes in the Soviet Union in the Journal of Physical Chemistry [7]. This finding was largely ignored because of the political situation. In fact, Radushkevich and Lukyanovich are credited with discovering that carbon filaments can be hollow and have nanoscale diameters -- the discovery of carbon nanotubes [6], [8]. John Abrahamson presented evidence for carbon nanotubes at the biennial 14th Carbon Conference at Pennsylvania State University in 1979. The conference paper describes carbon nanotubes as carbon fibers produced on a carbon anode during arc discharge and gives the properties of these fibers and the hypothesis that they grow in a low-pressure nitrogen atmosphere [9]. Lijima reported multi-walled carbon nanotubes in the insoluble material of arc burning graphite rods [2]. Mintmire, Dunlap, and White all forecasts suggest that if you can produce single-walled carbon nanotubes, then they will show excellent conductivity that have later debates about the origins of the carbon nanotubes [10]. IBM Bethune and Japan's electric Lijima in a separate study, in the process of arc discharge are added to the carbon, transition metal catalysts to specializing in the production of nanotubes for later research will greatly accelerate the nanotubes, arc discharge technique in the preparation of buck Munster fullerenes is famous for mass production [1], [11], [12]. These results appear to extend the scope of the serendipitous discovery of fullerenes. The discoverer of nanotubes remains a subject of great controversy. The Lijima's 1991 report is considered by many to be crucial because it made the entire scientific community aware of the existence of carbon nanotubes [6]

Application of CNTs

Since Lijima's research in 1991 focused scientists' attention on carbon nanotubes, which have been developed for many applications due to their excellent mechanical and electrochemical properties, and up to now, carbon nanotubes have a wide range of application prospects. Easy-Bell Sports worked with Zyvex Performance Materials, in order to use carbon nanotube technology in bike components, such as riser handles, forks, cranks, seat bars, and air bars. Amory Europe Oy manufactures Hyperite Carbon Nanocup Hydrogen Resin, in which the carbon nanotubes have been chemically activated and bonded to acyclic hydrogen resin, thus forming composites that are 20% to 30% stronger than other composites. In this way, it can be used in wind turbines, marine paint, and a variety of sports equipment [6]. It is worth mentioning that the potential of carbon nanotubes in biomedical applications is infinite because of their electrochemical properties. Now carbon nanotubes are used as a scaffold for bone growth in tissue engineering [13]. This is because carbon nanotubes carrying neutral electric charge, which is sustained the highest cell growth and production of plate-shaped crystals. There is a dramatic charge in cell morphology in osteoblasts cultured on multi-walled nanotubes, which correlated which changes in plasma membrane. With further advancements, carbon nanotubes could also be used to repair neurons, which have an interest in neurological diseases and the study of brain [14], [15].

Synthesis of CNTs

Arc discharge method, laser ablation method, and chemical vapor deposition (CVD) method are three common methods to synthesis carbon nanotubes (CNTs). 3.1. Arc Discharge Method Arc discharge requires a high temperature to evaporate carbon atoms into plasma. When the pressure is about 50 to 700 mbar with inert gas atmosphere, an electric arc can be generated between two closely spaced graphite electrodes [16]. To form carbon plasma, the temperature needs to exceed 3000 Celsius. In order to improve the CNT yield and selectivity, it requires more theoretical study to understand CNT synthesis mechanism with plasma

techniques. With arc plasma, the flexible CNTs with fewer defects can be produced. The argon-helium-nitrogen-carbon-cobalt-nickel plasmas was usually used in CNT synthesis. In 2014, the net emission coefficient was calculated to investigate the radiative properties of this plasma in CNT synthesis at the assumption of a local thermodynamic equilibrium and at temperature range from 1000 K to 20,000K [17]. And two years later, this group calculated the mean absorption coefficients (MACs) for plasma mixtures of argon-helium-nitrogen-carbon-nickelcobalt using the same temperature range and at 60kPa of pressure [18]. They also present that absorption coefficient strongly depends on the photodissociation and photoionization process when the temperature is lower than 600K, and radiative recombination process contributes the most in continuum absorption coefficient, which except in the infrared region. This series of exploration of CNT synthesis mechanism with plasma techniques provides some clue to let researchers investigate further in the future.

Laser Ablation Method

Laser Ablation uses similar principle with arc discharge but use a laser as the energy source to heat the carbon target. Then the carbon target is vaporized and then condense in a carrier gas stream. The effect of laser wavelength was studied in synthesis of single-wall carbon nanotubes (SWCNTs) and its properties [19]. Their results showed that laser fluence strongly influence the growth condition of SWCNTs. The useful range of the UV laser radiation fluence is narrower, and the properties depend much more on the laser fluence than the infrared laser radiation. The boarder population distribution from their Raman spectra with the increasing fluence lead to a larger range of SWCNTs diameters. The large-scale of CNT can obtain under normal temperature and pressure by the pulsed laser ablation of graphite target in metal nano-sol [20]. The metal nano-sol plays the role of catalyst in the synthesis process, acting as the liquid medium.

Chemical Vapor Composition Method

Using CVD to synthesis CNT needs a transition metal catalyst to proceed a thermal dehydrogenation reaction. Chemical deposition method is a low-cost, high-yield, and easy-control method to produce CNT. Some researchers stated that CVD synthesized CNTs are not as good as arc charge or laser ablation synthesized CNTs, and cobalt, nickel, copper, and iron are commonly used as the catalyst, in order to separate the gaseous hydrocarbon into carbon and hydrogen by lowering the temperature [16]. Chen etc. produced multi-wall carbon nanotubes (MWCNTs) by using nano-MgNi under pyrolysis of pure CH4 gas at high temperature. This optimum reaction based on the methane conversion and carbon yield of CVD [21].

Table 1. Comparison of the Common Techniques for CNT Synthesis [16]

Method	Are Discharge	Laser Ablation	Chemical Vapor Deposition
Description	Arc evaporation of graphite in the presence of inert gas; CNT formed; CNT formed on electrodes during quenching	Vaporization of graphite target by laser; CNT formed on receiver during quenching	Decomposition of hydrocarbons over transition metal catalyst to form CNT.
Operating Temperature	>3000 °C	>3000 °C	>1200 °C
Operating Pressure	50-7600 Torr generally under vacuum	200-750 Torr generally under vacuum	760-7600 Torr

Advantages	Good quality	Good quality; single	Easy scale up; it is	
		conformation SWNT	possible to	
		formed;	synthesis on	
			templates;	
Disadvantages	Difficult to scale it up	Difficult to scale it up; expensive	Quality is not that good	

Properties

The properties of nanotubes depend on atomic arrangement, tube diameter and length, morphology or nanostructure. These cage-like forms of carbon showed that exhibit exceptional material properties are a consequence of their symmetric structure.

Electrical properties

Researchers have demonstrated that CNTs display extraordinary conductivity. The defects of the tubular structure, chirality, different diameters and crystallinity and other geometric differences greatly affect the electronic properties of CNTs[22], [23]. SWNTs show metallic properties with resistivity that range from 5.1 × 10-6 to 1.2 × 10-4 ohm cm [24]. Each carbon atom arranged in a hexagonal lattice covalently bonded to three adjacent carbon atoms through sp2 molecular orbitals. Therefore, the fourth valence electron remains free in each unit, and these free electrons delocalize on all atoms and contribute to the electrical properties of the CNT. Therefore, depending on the type of chirality, CNTs can be conductive type or semi-conductive type [22]–[27] carbon nanotubes exhibit electrical properties in chiral forms. The form of p-type semiconductors is existed in semiconducting singlewalled carbon nanotubes [28]. Multi-walled carbon nanotubes are not likely to be strictly onedimensional conductors because A number of single-walled carbon nanotubes composed in multiwalled carbon nanotubes [29]. The electrical properties of single-walled carbon nanotubes and multiwalled carbon nanotubes have been well studied. Due to the ballistic properties of electron transport, single-walled carbon nanotubes can be described as quantum wires. On the other hand, it is found that the transportation of multi-walled carbon nanotubes has considerable diffusivity or quasi-ballistic properties [30]. Carbon nanotubes can be used for switching applications in transistors and other advanced electronic technologies due to their electronic properties [31]. CNTs can also be used in biosensors, which is a micronscale on-chip triodes at a high frequency (>200 MHz), vacuum microelectronics, and for X-ray generation [32], [33]. Zhang et al. [34] found that the semiconducting selectivity of CNTs which grown as ultra long was higher than 92.6%, and their on/off ratio was as high as 4.8×106 , which can be expected even higher.

Mechanical properties

CNTs are considered as the strongest materials in nature due to the carbon- carbon bonds observed in graphite. The literature shows that CNT is a very strong material, especially in the axial direction [34]. Its Young's modulus is between 270 and 950 GPa, and the tensile strength is high as well, which is between 11 and 63 GPa. Some reports indicate that CNTs are quite soft in the radial direction [3]. Research on CNTs under TEM shows that these materials are flexible and will not break when bent. The results show that CNTs are actually soft in the radial direction. The radial elasticity is an important property, especially for the formation of CNT nanocomposites and the mechanical properties. When a load is applied to the composite structure, the embedded tube will deform greatly in the lateral direction [35]–[38]. Falvo et al. [39] explored that using the AFM tip, the MWNT can be bent into an acute angle without any structural fracture. Endo et al. [40] showed that when vaporgrown CNTs were destroyed in liquid nitrogen, the inner tube can withstand this pressure.

Zhu et al. [41] used a shock wave to apply a high voltage (50 GPa) at room temperature to arc the MWNT and pointed out that the tube would not break but would collapse. Sinnot et al. [42] conducted more theoretical studies on the mechanical properties of carbon nanotubes, they found that the Young's modulus and singlewalled carbon nanotubes may be as high as diamond. Yakobson [43] and Ru [44] proposed the mechanism of CNT transformation under uniaxial tension, which resulted in pentagonheptagon defects in these tubes under high stress. Theoretically, it is also shown that the mechanical properties of single-walled carbon nanotubes mainly depend on the diameter. Guanghua et al. [45] estimated that the theoretical Young's modulus of a nanotube with a diameter of 1 nm is in the range of 0.6-0.7 TPa. Hernandez et al. [46] also obtained the theoretical value of Young's modulus, which is very close to the experimentally obtained MWNTs (1-1.2 TPa). They also reported that the increase in its diameter is proportional to the increasing of the mechanical properties of CNTs. If the diameter increases to a certain value, the Young's modulus of the tube will be close to that of planar graphite. Yu et al. [3], [47] measured the Young's modulus of each single-walled carbon nanotube, and the reported value was between 320 and 1470 GPa, and determined that the perimeter of each singlewalled carbon nanotube ranges from 13 to 52. Breaking strength of GPa. Zhang et al. [34] experimentally demonstrated that as grown in centimetres long CNTs with perfect structures, it exhibited tensile strength which is higher than 100 GPa, and the breaking strain is higher than 17.5%, rendering them with an excellent mechanical energy storage capacity that is higher than 1000 Wh/kg.

Thermal properties

Carbon nanotubes are not only attracting attention in electrical and mechanical properties, but their thermal properties are also being studied. Due to the thermal conduction of nanometer materials plays a critical role in controlling the performance and stability of Nano and micro devices. Therefore, the thermal management in nano sized devices becomes increasingly important as the size of the device reduces.

Table-2 Some Properties of CNT [16]

Material	Units	SWCNT	MWCNT	References
Tensile Strength	GPa	75	150	[48]
Young's Modulus	GPa	900- 1700	1800 average, 690- 1700	[49],[50]
Resistivity	$\Omega \cdot \mathbf{m}$	10-6		[51]
Maximum Current Density	$A \cdot m^2$	107 - 109	7.27	[29]
Quantized Conductance, Theoretical	$(k\Omega)^{-1}$	6.5	JE!	[52]
Quantized Conductance, Measured	$(k\Omega)^{-1}$	12.9		[53]
Thermal Conductivity	W m ⁻¹ K ⁻¹	1750-5800	3000	[5],[53]

discussed thermal conductivity decreases as the vacancy concentration increases. Zhang et al. [34] explored the heat conductivity and transfer coefficient of the perfect CNTs in air, applied by noncontact Micro-Raman spectroscopy technique. The data confirm perfect CNTs have the highest thermal conductivity. Kim et al. [5] measured the thermal conductivity of MWNTs and found that its thermal conductivity was 3,000 W/K at room temperature, which is higher than that of graphite. Moreover, they also determined the value that is two orders higher than the magnitude those obtained for bulk MWNTs. Yu et al. conducted a similar study for single-walled carbon nanotubes, the thermal conductivity of each SWNT is 200 W/m K greater than that of each MWNT [56]. The specific heat and thermal conductivity of the carbon nanotube system are mainly determined by phonons. The contribution of phonons to these numbers plays a major role at low temperatures, which is mainly due to phonons. The linear temperature dependence can be explained by the linear kvector

790

dependence of the frequencies of longitudinal phonons and twisted phonons [57]. The specific behavior of specific heat below 1K can be attributed to the lateral phonons with quadratic kdependence [58].

Conclusion

The history, synthesis, different applications as well as materials properties of CNTs were reviewed in this paper. The important methods of synthesizing carbon nanotubes (SWNT and MWNT) are briefly discussed, including arc discharge method, laser ablation method and CVD method. Some extraordinary properties of CNT are also reviewed and introduced, and the conclusion is drawn that CNTs have a series of electrical, mechanical and thermal properties. In the future, it is obvious that new technologies will appear in terms of the greatest potential of CNTs. However, the problems associated with these technologies are the production, subsequent purification, and cost of CNTs.

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