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Synthesis and modification of carbon nanotubes

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Abstract. Carbon nanotubes (CNTs) are mono-dimensional carbon nanomaterials with remarkable properties. Since their discovery by Iijima, they have been found to exhibit remarkable properties in mechanical, physical, and chemical fields. However, due to their harsh synthesis conditions and limited inherent properties, the large-scale application of CNTs is challenging. With the aim of providing a reference for further research and development of carbon nanotubes, this review summarizes the currently reported methods for synthesizing carbon nanotubes, focusing on the cost-effective arc-discharge method and chemical vapor deposition (CVD) which produce high-quality carbon nanotubes with stable performance. In addition, two different directions of CNT modifications are presented, namely, CNT filling technology and CNT solubility modification. Among them, the CNT filling technology can use CNTs as templates for nanodevice fabrication and test tubes for microscopic reactions. Meanwhile, solubility modification of CNTs is the key strategy to overcome its inherent limitations and expand their application fields.

Keywords: CNTs, arc-discharge, CVD, modifications.

1. Introduction

Carbon-based nanoscale materials have made significant contributions due to their outstanding unique properties. Among the carbon nanomaterial families, the well-known mono-dimensional material, carbon nanotubes (CNTs), have been widely studied for their surprisingly high tensile strength, high thermal conductivity, and variable electron conductivity, etc.

CNTs can be thought of as a composite of one or more layers of rolled-up graphene sheets. These tubes are named as single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs), respectively. In terms of crystallography, carbon tubes can be classified into three distinct structural categories: zigzag, armchair, and chiral. The hexagonal crystal structure of CNTs makes the carbon atoms in them exhibit sp2 hybridization. And the curved σ bonds which are caused by the curvature of the cylindrical structures and a small number of crystal defects, make CNTs also partially show sp3 hybridization characteristics as well.

The preparation of CNTs and their inherent chemical properties are two major obstacles that have prevent them from expanding their applications. The synthesis of CNTs often requires high temperature, high pressure and catalysts, which make them difficult to scale. The superhydrophobicity, high oxidability and easy agglomeration of CNTs make it difficult to use in fields like biochemistry and catalytic chemistry. With different modifications applied, the potential of CNTs could be greatly unlocked.

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Based on the above reasons, this paper focuses on the two most commonly used CNT synthesis methods, the arc-discharge method and the chemical vapor deposition (CVD) method and describes their synthesis genres and common catalysts. Two modification strategies of CNTs, CNT filling and CNT solubility modifications, are also introduced. Some chemical modifications of CNTs, such as oxidation, polymer coating, etc., are presented as well. This is of interest to the newcomers and future researchers in this field.

2. Synthesis of CNTs

Although the mechanism of the generation of carbon nanotubes is to be ambiguous, while multiple synthesizing methods are reported.

The first officially reported CNT was discovered in the deposits on the graphite cathode by Iijima in 1991, and arc discharge has been confirmed as the first recorded CNT synthesis method [1]. With the same mechanism "vaporization of graphite and reassembly of carbon atom plasma into nanotubes", laser ablation, solar production, etc. were reported one after another. Apart from the carbon evaporation mechanism, they can be synthesized by chemical vapor deposition as well. The CVD method has been widely used by researchers due to both the simplicity of the equipment required and the high quality of CNT products with stable performance. There are other reported CNT synthesis methods, such as electrochemical synthesis and graphite powder ball-mining annealing. However, they are not as widely used as the two methods mentioned above due to the immature technology or low yield.

2.1. Arc-discharge method

The arc-discharge technique was originally discovered by Krätschmer et al. for producing fullerenes in large quantities, and a Krätschmer reactor was invented for applying arc discharging reaction. A classic Krätschmer reactor consists of a vacuum chamber as the reaction space, graphite electrodes as carbon precursor, a graphite or copper cathode, and an arc welder to initiate the arc. With the discovery of CNTs in the remains of the reaction products, the Krätschmer reactor and its modifications were also used for the preparation of CNTs.

To operate an arc discharge, the vacuum chamber must be completely evacuated and injected with low pressure inert gas or certain reactive gas like hydrogen. The cathode and graphite anode should be placed at a distance of 1 mm. A low voltage, high current DC is then applied between the two electrodes to generate an arc made of high temperature, high energy plasma between the electrodes. During the discharge process, the graphite anode will be continuously atomized due to the high-temperature plasma bombardment to form CNTs or other carbon isomers. The distance between the graphite electrodes should be held the same as it is when the arc is started by pushing the anode forward to maintain the arc to keep the reaction going. At the end of the reaction, i.e., after the anode is completely consumed, CNTs can be collected on the vacuum chamber wall or in the cathode deposit.

Either single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) can be fabricated through arc discharging. Researchers can adjust the product properties and yield by controlling the ambient atmosphere, discharge current, cathode material and doping catalysts into the reaction system. Among them, the ambient atmosphere and catalysts have the greatest influence on the reaction products.

The commonly used ambient gases in the experiments are helium, argon, hydrogen, nitrogen, etc. Different types of environmental atmospheres make the mechanism of the generation of CNTs completely different, resulting in different morphologies of the products, e.g., Zhao et al. believe that hydrogen effectively promotes the formation of CNTs compared to helium since the generation of hydrocarbons reduces the generation of other carbon isomers [2]. The pressure inside the chamber also affects the generation of CNTs: when the pressure is too low, there will be a lack of sufficient plasma to sustain the arc; when the pressure is too high, the higher ion concentration will stunt the generation of CNTs as well. Typically, researchers control the pressure during the reaction to around 40 to 90kPa.

In absence of a catalyst, the arc-discharge method only allows MWCNTs to form, yet a catalyst can not only turn the product into SWCNT and enhance the yield of CNTs but can also enhance the length

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of CNTs. Generally, the catalyst is composed of transition metal oxides such as Fe, Ni, Co, or rare earth oxides or metal oxides components. The catalyst will be mixed and doped with graphite and made into a composite anode. For example, graphite anode prepared by doping with 2%wt of Co-Ni catalyst can yield SWCNTs with purity up to 70% at the chamber wall [3].

2.2. Chemical vaper deposition

CVD was first introduced as a chemical synthesis concept in the 1960s by JM. Blocher Jr. et al. in the book "Vapor Deposition", but has been used in composite coatings, semiconductor fabrication, and other applications long before that.

Today, CVD is a widely used and simple method for synthesizing CNTs. Equipment for CVD fabrication of CNTs usually consists of a gas source control component, a deposition chamber, and a vacuum exhaust and pressure control component. In a typical CVD reaction process, carbon-bearing gases such as acetylene, benzene, methane, etc., mixed with carrier gases such as argon, etc., are introduced into a deposition chamber heated to 700-900 ℃, where the carbon source is pyrolyzed and deposited on the surface of the catalyst, initiating the growth of the CNTs.

Catalysts are critical for CNTs to grow within the deposition chamber, and transition metals such as Fe, Co, and Ni are currently the most applied catalysts due to their high carbon solubility. Currently, CVD can be categorized into two types based on how the catalyst is supplied or presented: seeding method and floating catalyst method.

The seeding method is to deposit the catalyst uniformly on a flat substrate such as silicon wafer, sapphire, etc. by physicochemical methods, such as the sol-gel method and impregnation method. The deposited substrate is then placed into the deposition chamber, and CNTs start growing on the surface of it. This method can be implemented by lattice-induced orientation or by applying an external field or force for the directional growth of CNT arrays.

The floating catalyst method is based on mixing a catalyst precursor with a carbon source and introducing it into the reaction zone, where the catalyst precursor decomposes into nanoparticles at elevated temperatures. The saturated carbon on the surface of the nanoparticles precipitates out and continue to grow to form CNTs. There are various ways of mixing the catalyst and the carbon source, which include injecting the catalysts, or even direct use of a gaseous catalyst. Today's floating catalysts are usually organometallic compounds such as metallocenes and carbonyls.

3. Modifications of CNTs

It is true that CNTs have excellent properties such as high tensile strength, high electrical conductivity, and surface inertness, but on the other hand, these advantages are like a double-edged sword limiting their applications to a wider range of fields. Physical or chemical modification is the key to the wider application of carbon nanotubes, which can explore new fields and directions for the application of CNTs and improve the added value and performance of them.

3.1. External substance inside a nanotube

The molecular structure of a CNT is hollow, and the nanoscale space inside them could carry external substances, and the interaction with molecules adsorbed in them is greatly enhanced. As a result, the reactivity inside CNTs is very different from that of the outside. On the other hand, the hollow structure of it also makes them important templates for the construction of nanocomplexes, nanodevices, and even mono-dimensional nanowires.

Many kinds of substances and their compounds are known to have been successfully filled into the inner space of CNTs, including transition metals, nonmetals, quasimetals, lanthanides, actinides, and even fullerenes, endohedral fullerenes, and biomolecules. To fill the above-mentioned substances, the currently reported methods can be divided into three groups: encapsulation during preparation, physical filling by capillary effect, and chemical filling.

The direct synthesis of encapsulated CNTs, or nanopods, is currently one of the most effective ways to prepare such materials in large quantities and with high efficiency. The known methods of direct

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synthesis are through arc discharge and through CVD. Preparing nanopods by arc discharge method involves the preparation of electrodes by doping metals or their compounds with graphite for discharge synthesis. This method yields both completely uniformly filled CNTs and partially discontinuously filled CNTs. The difference in the result is not only related to the reaction conditions, such as temperature in the chamber, but also to the type of metal. Catalytic pyrolysis is a method in which an excess of metal catalyst is introduced into the reaction system during the CVD process, and the CNTs will grow on the surface of molten metal catalyst and encapsulated the metal therein to form nanopods.

The capillary effect method uses opened CNTs as capillaries to induce external substances into the hollow space. Low surface tension substances such as lead oxide and vanadium pentoxide can be introduced into the CNTs, while high surface tension substances such as lead or bismuth can be introduced by first reacting with oxygen or carbon to form low surface tension substances as well. Co-fusion of solid phase fillers with carbon nanotubes produces continuous nanowires.

The chemical method uses the introduction of external substances into the interior of CNTs in the form of salts at a lower temperature (140 °C). A wider variety of substances of metal can be filled through this method rather than the capillary effect method, which includes not only pure metals but also metal oxides. However, only discontinuously filled CNTs can be synthesized with this method.

3.2. Soluble carbon nanotubes

The concept of CNT modification comes from the idea of soluble modification of CNTs. Due to the inherent property of CNTs, they are neither soluble in water nor organic solvents, which greatly limits the study on their chemical, optical, and other properties. To make CNTs soluble in solvents, researchers have reported on two different modifications, which are the chemical modification and the polymer modification, respectively.

The hyperconjugated π-electron system in the walls and the high tensile strength of the carbon rings in the endpoint make the modifications of CNTs possible. They can be either introduced with functional groups on the walls or their chemically sheared ends. By using common oxidizing agents such as nitric acid, hydrogen peroxide, permanganate, etc., CNTs can be functionalized with oxygen-containing groups such as carboxyl and carbonyl groups on their surface just like graphite. The water solubility of CNTs can be improved when the surface is modified with the above functional groups through covalent bonding, hydrogen bonding, etc. Zhao et al. found oxidized CNTs can form a solution and stabilize for 12h when pH is lower than 3 [4]. On the other hand, long-chain alkyl groups, amines, DNA, etc. can be introduced to the open ends of CNTs, so that they can be soluble in organic solvents, and sometimes their water solubility can also be improved.

The use of coating CNTs with polymer is a new type of modification, which does not change the property of CNTs through covalent bonding, but can still change their wettability, electrical conductivity and many other properties. In situ polymerization of carbon nanotubes with different monomers, according to the different affinity of different monomers for solvents, CNTs with affinity for corresponding solvents can be obtained. For example, in situ polymerization of MWCNTs with phenylacetylene can make carbon nanotubes have good solubility in a variety of organic solvents [5]. The solubility of SWCNTs coated with soluble straight-chain starch can reach 3 g/L in water [6].

4. Conclusion

This paper reviews carbon nanotubes, a nanomaterial that is challenging to synthesize and apply, and promises great potential. This paper describes two synthesis methods: arc discharge and chemical vapor deposition, and compares their advantages and disadvantages. The article also describes two modification methods: cavity filling and solubility enhancement, and discusses their impact on expanding the application range of CNTs and exploring their relevant properties. Other important aspects of CNTs such as purification methods, characterization, mechanical and electrical properties are not covered. The introduction of the synthesis methods is not exhaustive, and other modification strategies of CNTs are not mentioned due to space limitation.

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In conclusion, the main tasks of CNT science in the coming period are to increase its yield and reduce its production cost, as well as to improve the properties of carbon nanotubes themselves through covalent or non-covalent functionalization, with the aim of playing a more important role in the cutting-edge interdisciplinary disciplines in various fields.

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