Preparation and Application Research of Carbon Nanotubes

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Keywords: Carbon Nanotubes, Chemical Vapor Deposition (CVD) Method, Laser Ablation Method, Arc Discharge Method, Lithium Batteries.

Abstract: In recent years, carbon nanotubes have shown broad application prospects and become the research frontier and hotspot in the international new materials field. This paper mainly discusses the classification, mechanical, and electrical properties of carbon nanotubes and their preparation methods, and analyzes their application examples in fields such as lithium batteries. The results show that the mechanical properties of carbon nanotubes are far superior to traditional materials and they also have excellent electrical properties. Regarding the preparation methods of carbon nanotubes, the arc discharge method is simple, fast, and high-yield, the laser ablation method has relatively higher costs, while the equipment used in chemical vapor deposition (CVD) method is simple and capable of large-scale production. In practical applications, carbon nanotubes have achieved results in areas such as cathode materials in lithium batteries, solid-phase extraction adsorbents, and catalytic materials. This study holds significant practical significance in exploring low-cost, large-scale production of carbon nanotubes and provides a scientific basis for their future applications in other fields.

1 INTRODUCTION

In 1991, Professor Iijima, an electron microscopy expert from a Japanese electronics company, discovered for the first time under a high-resolution transmission electron microscope some needle like structures composed of 2-50 concentric tubes, while preparing C60 using an arc method μm. This is carbon nanotubes.

Carbon nanotubes are a type of material with a radial size in nanometers and an axial size in micrometers, which has a structure different from other materials. The hexagonal carbon atoms form the carbon nanotubes, which curl along certain axes to form coaxial circular tubes. The distance between carbon atomic layers is about 0.34 nm, with most diameters ranging from 2-20 nm. It is precisely because its many properties, such as mechanical properties, are better than other materials that it has been widely used and has attracted the attention of scientists in many fields.

This article analysed and studied the preparation and application of carbon nanotubes. Firstly, the classification of carbon nanotubes and their mechanical and electrical properties were explained. Then, the preparation of carbon nanotubes was introduced from three methods: arc discharge method, laser burning method, and chemical vapor deposition method. Finally, the application examples of carbon nanotubes in lithium batteries, fuel cells, and other fields were elaborated.

2 CLASSIFICATION OF CARBON NANOTUBES

2.1 Single Walled Carbon Nanotubes

The incredible strength and flexibility of single-walled carbon nanotubes (SWCNTs) make them a fascinating material for researchers and engineers. These nanotubes are entirely composed of carbon atoms. Their shapes are mainly divided into armchairs, serrations, and chirality, each with its own unique electronic properties.

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Zhang, M. and Zhang, S.
Preparation and Application Research of Carbon Nanotubes.
DOI: 10.5220/0013847500004914

In *Proceedings of the 2nd International Conference on Renewable Energy and Ecosystem (ICREE 2024)*, pages 103-108
ISBN: 978-989-758-776-4

When it comes to mechanical properties, carbon atoms in SWCNTs are bonded through extremely strong C-C covalent bonds, indicating flexibility. In addition, these nanotubes exhibit incredible high axial strength, approximately 100 times that of steel. Their elastic strain can reach up to 5%, with a maximum of 12%.

SWCNTs have received much attention for their superior properties and applications in composites. SWCNTs can give composites extraordinary mechanical properties, significantly improving their strength, toughness, elasticity and fatigue resistance. SWCNTs also possess properties including anisotropy and diamagnetism. SWCNTs have extremely strong capillary action and wetting features. They are the materials with the largest hydrogen storage capacity that are expected to promote the development of hydrogen fuel cells compared to other traditional hydrogen storage materials.

2.2 Multi Walled Carbon Nanotubes

Carbon nanotubes are connected by stable C=C covalent bonds and thus have excellent mechanical properties. Theoretical calculations indicate that carbon nanotubes have extremely high strength and toughness. The theoretical value estimates that the Young's modulus can reach 5 TPa, with a strength about 100 times that of steel, while the weight density is only 1/6 of steel. Treacy et al. used Transmission Electron Microscope (TEM) for the first time to measure the mean square amplitude of multi walled carbon nanotubes in the temperature range from room temperature to 800 degrees.

3 PERFORMANCE OF CARBON NANOTUBES

Carbon nanotubes are a type of nanomaterial with excellent performance and broad application prospects, and their unique structural characteristics determine their potential for application in multiple fields. Carbon nanotubes, as an important nanomaterial, have many unique properties, including structural characteristics, mechanical properties, electrical properties, and thermal properties. Studying its performance will help promote the application of nanomaterials in various fields.

3.1 Mechanical Properties

The mechanical properties of carbon nanotubes refer to their mechanical response and performance under external forces. When studying the mechanical properties of carbon nanotubes, indicators such as elastic modulus, yield strength, fracture strength, and tensile properties are usually considered.

Carbon nanotubes have excellent elastic modulus, usually above 1 TPa, and even up to hundreds of TPa. This makes carbon nanotubes have important application potential in fields such as nanomaterial reinforcement and nanocomposites. The introduction of carbon nanotubes (CNTs) into NC will reduce the percolation threshold and resistivity of composite materials, and improve the tensile strength of composite materials (Zhang et al., 2024).

Due to the nanoscale characteristics of carbon nanotubes, their yield strength is usually much higher than traditional materials, reaching tens of GPa or even higher. This makes carbon nanotubes have important application prospects in fields such as nanodevices and nanosensors. Meanwhile, due to the influence of structural defects, external environment, and other factors on the yield behaviour of carbon nanotubes, researchers are also committed to exploring the yield behaviour laws and influencing factors of carbon nanotubes, in order to better apply them in engineering practice.

3.2 Electrical Performance

Carbon nanotubes have good electrical properties due to their helical tubular structure. Research has shown that the current carrying capacity of single-walled carbon nanotubes is 1000 times that of copper, approximately 109A/cm2.The conductivity of single-walled carbon nanotubes also changes with the change of their diameter and helical mode. CNTs dispersed in polymer matrices are more likely to form conductive networks, and composite materials prepared with CNTs as conductive fillers have a percolation threshold of less than 5%, or even less than 1% (Qiu et al., 2020).

3.3 Thermal Conductivity

Like conductivity, carbon nanotubes are also excellent thermal conductors, with an axial thermal conductivity of approximately 6600 W/m·K or higher, far greater than diamond and graphite. Their application in composite materials more extensive, and the study of their properties and applications has important theoretical and practical significance

(Zheng et al., 2024). It can become a thermal conductive agent for the heat sink of Central Processing Unit (CPU) chips in computer central processing units. The carbon nanotube CPU heat sink produced by OCZ Company, as shown in Fig. 1, is a physical image of the central processing unit and an example of the CPU. Its thermal conductivity efficiency is 5 times that of ordinary copper materials. In addition, single-walled carbon nanotubes can also be used in high thermal conductivity composite materials, with good application prospects.

Figure 1: Physical image of central processing unit (Chen et al., 2024).

4 CARBON NANOTUBE PREPARATION METHODS

4.1 Arc Discharge Method

The main principle of the arc discharge method is to place an anode and a cathode in a vacuum-sealed container, fill it with an inert gas such as argon, and apply a high voltage between the two poles to generate an arc, creating high temperature and high pressure conditions. In the high temperature environment, carbon arc discharge generates high energy, causing some atoms on the surface of the conductive material to evaporate and ionize to form high-energy ions. At the same time, the polarity of the carbon source determines the type of product. Ultimately, carbon atoms transfer in a free state at high temperature and high energy under the action of electrons and ions, condense, and deposit on the cathode surface, forming carbon nanotubes. The earliest carbon nanotubes were accidentally obtained during the conventional arc discharge process used for preparing fullerenes. In 1991, Iijima obtained carbon nanotubes through arc discharge technology in an argon environment (Iijima, 1991). In 1992, Ebbesen et al. (1992) significantly increased the yield of carbon nanotubes by increasing the helium gas pressure in the arc chamber, reaching a level of kilograms, making arc discharge one of the primary methods for mass-producing carbon nanotubes. In 1993, Iijima and Ichihashi introduced a small amount of transition metal iron into the graphite anode and synthesized single-walled carbon nanotubes through arc discharge in a methane and argon atmosphere (Iijima, 1993).

The advantages of the arc discharge method are its simplicity, speed, high yield, and high degree of graphitization. Moreover, the carbon nanotubes produced by this method exhibit excellent properties. However, the arc discharge in this method is often very intense, making it difficult to control the process. Additionally, carbon nanotubes in the deposition on the cathode during arc discharge are prone to sintering, resulting in the presence of numerous carbon nanograins. Fig. 2 shows the device for preparing carbon nanotubes by arc discharge method.

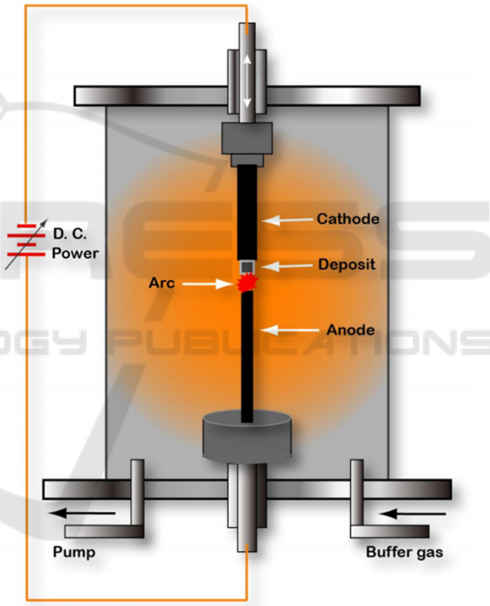

Figure 2: Arc discharge apparatus for preparing CNTs (Zhao, 2014).

4.2 Laser Ablation Method

This method was first discovered by Smalley et al. (Guo et al., 1995), involves using high-energy lasers as a heat source in an inert gas environment to vaporize solid graphite for the synthesis of carbon nanotubes. Initially, the graphite target is placed in a tube furnace and heated to 1200 ℃. The laser vaporizes the graphite target, which is then carried by a carrier gas to a copper collector equipped with a wate cooling device, where carbon vapor condenses and grows on the cooled surface, forming carbon nanotubes. Laser ablation method allows for the control of carbon nanotube diameter by adjusting the reactor temperature. However, the use of high-energy lasers increases its cost compared to the arc discharge method and chemical vapor deposition method. Fig. 3 illustrates a schematic representation of the equipment used in the laser ablation method for synthesizing carbon nanotubes.

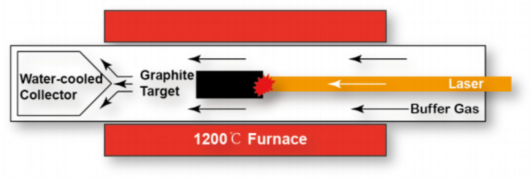

Figure 3: Schematic representation of a laser vaporization apparatus for preparing CNTs (Zhao, 2014).

4.3 CVD Method

Chemical vapor deposition is a process that utilizes gaseous substances to undergo chemical reactions on a solid surface, leading to the deposition of gaseous products. In the context of carbon nanotube synthesis, CVD involves the catalytic cracking and deposition of carbon-containing gases on catalyst particles at temperatures ranging from 700 ℃ to 1000 ℃ within a high-temperature tube furnace filled with a carbon source and carrier gas.

Common carbon sources used in CVD include ethylene, acetylene, ethanol, among others, while commonly used carrier gases are mixtures of hydrogen and argon. The Smalley research group, for example, employed CO as the carbon source and ferrocene as the catalyst, conducting continuous synthesis of high-purity single-walled carbon nanotubes with a diameter of 0.7 nm at temperatures ranging from 1073 to 1473K and pressures from one to ten atmospheres (Nilolave et al., 1999).

The equipment used in the CVD method is known for its simplicity, easy controllability of conditions, scalability for large-scale production, and the ability to directly grow carbon nanotubes on suitable substrates. Fig. 4 is a CVD apparatus for growing CNTs.

Figure 4: Schematic representation of a CVD apparatus for growing CNTs (Zhao, 2014).

5 APPLICATIONS OF CARBON NANOTUBES IN PRACTICE

Carbon nanotubes possess unique electrical conductivity, mechanical properties, and physicochemical properties, which have attracted widespread attention since their inception, and in recent years, they have been widely applied in numerous scientific research fields.

5.1 Applications in Lithium Batteries

Lithium-ion battery performance indicators such as capacity and voltage largely depend on the performance of the cathode material. However, common cathode materials like lithium iron phosphate and lithium cobalt oxide suffer from low electrical conductivity, poor rate capability, and cycling stability issues (Shi and Ding, 2012). These problems mainly stem from structural changes occurring within the material during the repetitive lithium-ion intercalation and deintercalation processes. Simultaneously, there is a decrease in electron transport capability, ultimately leading to cathode material pulverization and increased internal resistance (Lu, 2022).

Carbon nanotubes exhibit excellent electron conductivity and mechanical properties. They not only provide good electron transport pathways for cathode materials but also further enhance the electrode's mechanical performance. Consequently, carbon nanotubes are widely used in cathode materials. Due to their superior electrical conductivity and ion diffusion capabilities compared to traditional materials like carbon black, carbon nanotubes are commonly used as conductive additives in cathode materials. Additionally, high-strength carbon nanotubes can also enhance the mechanical performance of electrodes.

Yang et al. prepared a LiFePO4@CNT composite material with core and shell structure. By reducing the radius of LiFePO4, the process can greatly reduce the transmission path of lithium ions. At the same time, the introduction of CNT can improve the conductivity of the electrode material. The electrode material is recycled at a large doubling rate of 50 C, and the specific discharge capacity can still reach 65 mAh/g.

5.2 Applications of Solid Phase Extraction Adsorbents

Carbon nanotubes have a large specific surface area and strong adsorption capacity, making them promising materials for solid-phase extraction. Literature reports indicate that carbon nanotubes exhibit high enrichment capabilities for organic compounds (Liang et al., 2004), metal ions (Muñoz et al., 2005), organic metal compounds (Cai et al., 2003), and other environmental pollutants. Cai et al. employed multi-walled carbon nanotubes to enrich organic pollutants from environmental water samples, such as bisphenol A, 4-nonylphenol and 4-octylphenol. The results showed that multi-walled carbon nanotubes had high enrichment efficiency, surpassing or equaling that of solid-phase extraction adsorbents like C18-bonded silica gel, XAD-2 resin, and C60 fullerene (Liang et al., 2004; Cai et al., 2003 & Cai et al., 2005).

The development of novel adsorption devices based on carbon nanotubes is becoming a research hotspot in this field. Yuan Dongxing et al. (2004) tested the performance of multi-walled carbon nanotubes for enriching volatile organic pollutants and compared them with common adsorbents Carbopack B and VOCARB 3000, demonstrating the superior enrichment performance of carbon nanotubes. Saridara et al. (2005) used ethylene and carbon monoxide as carbon sources to generate carbon nanotube films on the inner surface of stainless steel using chemical vapor deposition and fabricated them into microtrap devices for volatile organic compound detection. Experimental results showed that carbon nanotubes synthesized from ethylene had higher density and larger adsorption capacity, exhibiting strong adsorption capabilities for volatile organic small molecules.

5.3 Applications in Catalyst Materials

Due to recent advancements in the functionalization of carbon nanotube walls, coupled with their excellent electron conductivity, unique adsorption and desorption properties towards reactants and reaction products, special spatial stereoselectivity in pore structure, strong metal-carbon interactions in carbon-metal catalysts, as well as the specific catalytic and photocatalytic properties induced by quantum effects in carbon nanotubes, along with their strong oxidizing and reducing capabilities, there has been considerable interest in the application of carbon nanotubes in catalytic chemistry. Currently, there are not many examples of direct utilization of carbon nanotubes as catalysts. Lou et al. reported the direct application of carbon nanotubes with a surface area of 180 m2/g in the catalytic reduction of NOx, achieving 8% conversion of NO at 573K, which increased to 100% at 873K. This represents a successful application of nanomaterial quantum effects in catalytic chemistry. Carbon nanotubes are mainly used as carriers in catalytic processes due to their unique electronic properties, pore structure and adsorption capacity. Planeix was among the first to utilize carbon nanotubes as catalyst supports. They found that catalysts with multi-wall carbon nanotubes loaded with Ru exhibited up to 90% selectivity and an 80% conversion rate in the hydrogenation synthesis of cinnamaldehyde to cinnamyl alcohol.

6 CONCLUSION

Carbon nanotubes possess unique electrical conductivity, mechanical properties, and physical and chemical properties, making them widely applied in various scientific research fields in recent years. Carbon nanotubes mainly include single-walled carbon nanotubes and multi-walled carbon nanotubes. The mechanical properties of carbon nanotubes far exceed those of traditional materials, reaching tens of GPa, while also exhibiting excellent electrical conductivity, making them excellent thermal conductors.

Among the methods for preparing carbon nanotubes, the arc discharge method offers the advantages of simplicity, speed, and high yield, while the laser ablation method incurs relatively higher costs. On the other hand, the equipment used in CVD method is simple and capable of large-scale production. Currently, carbon nanotubes are widely used as cathode materials in lithium batteries, showcasing broader application ranges and higher mechanical performance. Additionally, their application as solid-phase extraction adsorbents presents promising prospects. However, there are relatively few examples of direct application of carbon nanotubes in catalytic materials.

In the future, researchers should focus on improving the existing shortcomings of carbon nanotubes and developing more diverse applications to achieve their large-scale utilization. This study holds significant practical significance in exploring low-cost, large-scale production of carbon nanotubes and provides a scientific basis for their future applications in other fields.

AUTHORS CONTRIBUTION

All the authors contributed equally and their names were listed in alphabetical order.

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