

Doping Modification of Carbon Nanotubes and its Applications

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Abstract: Buckytubes, a different term for carbon nanotubes, are quantum materials in one dimension that have a distinct structure. As one-dimensional nanomaterials, carbon nanotubes exhibit unusually broad mechanical, chemical and electrical capabilities in addition to their light weight and flawless hexagonal structural connectivity. Good mechanical capabilities, electrical conductivity, great chemical stability, a vast surface area, and a distinctive one-dimensional structure are all characteristics of carbon nanotubes. Doping is typically used to describe the small-scale addition of other elements or compounds to a material or matrix in order to enhance the performance of a certain substance or material in the chemical industry, materials, and other industries. A material or substrate can produce unique electrical, magnetic, and optical properties through doping. The abilities of the carbon nanotubes can be modified in a variety of ways by the addition of a trace amount of certain impurities. After doping in it, it can show many excellent properties, and can be widely used in various fields. In this work, doping modification of carbon nanotubes and its applications were studied.

Keywords: Carbon nanotubes, Doping modification, Application.

1. Introduction

Buckytubes, another name for carbon nanotubes, are unique one-dimensional quantum materials. Hexagonal carbon atoms, which are arranged in a few to tens of layers thick coaxial circular tube, make up the majority of carbon nanotubes. The diameter is typically 2–20 nm, and the gap between layers is kept constant at a distance of roughly 0.34 nm. Additionally, the hexagon can be classified into three different forms based on how it is oriented along the axis: zigzag, armchair, and spiral. In contrast to the zigzag and armchair, the helical is chiral.

The form of one-dimensional nanomaterials, carbon nanotubes are extremely light, precisely linked into a hexagonal structure, and have a wide range of unusual qualities that are mechanical, electrical, and chemical. During the previous years, as research into carbon nanotubes and other nanomaterials has progressed, it has become clear that these materials have a wide range of potential applications. Good mechanical capabilities, electrical conductivity, great chemical stability, a vast surface area, and a distinctive one-dimensional structure are all characteristics of carbon nanotubes. Choosing appropriate preparation method can enhance the physics performances of CNTs, thus making it great application prospects in many fields, especially in the application of the energy storage battery. Compared with graphite, carbon nanotubes have unique advantages in anode materials for lithium-ion batteries. First off, carbon nanotubes have a small-size influence on nanomaterials, which may effectively improve the reactivity space of lithium ions in the chemical power supply. The size of carbon nanotubes is at the nanoscale, as are the tube and intergap space. Secondly, the significant surface area of carbon nanotubes can increase the reactive active sites of lithium ions, and with the reduction of the diameter of carbon nanotubes, it shows a non-chemical equilibrium or integer coordination valence, and the storage capacity of lithium increases. Third, because of their high electrical conductivity, carbon nanotubes are able to embed and expel lithium ions more quickly, increasing the free transfer speed. This property plays a crucial role in facilitating high-power charging and discharging of lithium batteries.

The use of the conducting material is anticipated to rise in response to the increased demand for power worldwide. Until recently, electricity has been transferred using a conductor made of copper. Alternatives have been investigated because it is anticipated that in the near future, copper use will exceed its reserve. Due to its remarkable qualities, including chemical inertness, mechanical strength,

and electrical conductivity [1], carbon nanotube (CNT) has garnered increasing attention for decades. CNT yarn (or fiber) has great promise for replacing copper wires as a light-weight conducting material.

The properties of carbon nanotubes still need to be adjusted in the face of the increasingly demanding requirements of materials with the rapid development of various fields. Therefore, in this work will focus on various kinds of doping methods and the important applications of those different modified carbon nanotubes.

2. The doping modification of carbon nanotubes and its various applications

Doping is the term for mixing several substances. Doping is typically used to describe the small-scale addition of other elements or compounds to a material or matrix in order to enhance the performance of a certain substance or material in the chemical industry, materials, and other industries. A material or substrate can produce unique electrical, magnetic, and optical properties through doping, giving it a particular value or purpose.

As coiled graphene sheets, carbon nanotubes can be categorized into single-walled and multi-walled varieties depending on how many graphene sheets are present in each layer.

2.1 Single-walled carbon nanotubes

Compared to tubes with multiple walls, single-walled tubes possess a narrower diameter range, less flaws and greater regularity. The standard single-walled tube diameter is 0.6-2nm.

Single-walled carbon nanotubes (SWCNT or SWNT) are all composed of carbon atoms. The geometric structure can be regarded as a coiled monolayer of graphene, and the structure determines the properties. Therefore, SWCNT have excellent electronic, mechanical and mechanical properties. According to the coiled-coil structure, SWNTS have three types: armchair type, sawtooth type and chiral type. According to the electronic structure, SWNTS have semiconductor type and metal type. SWNTS have excellent electronic, mechanical and mechanical properties. At the same time, the change of the atomic scale can lead to the change of the properties of SWNTS. The resulting diversity of properties of SWNTS makes them potentially useful in many fields, including conductive films, infrared emitters, sensors, scanning probe tips, high-mobility transistors, logic circuits, field emission sources, high-mobility transistors, mechanical strength augmentation, solar cells, and catalyst supports.

Doping is a method of carbon nanotube modification that is frequently utilized. SWNTS, like graphite and some conjugated polymers, can be injected or doped into electron acceptors or donors. Many of the properties of the resulting materials are similar, including increased conductivity, conductive electron paramagnetism, partial or total reversibility, and cyclicity. The reaction might happen in a liquid, gas, or electrochemical phase. Due to the low quality of the currently accessible materials and the restricted effects of the solvents, structural information is, at best, hazy. Condensed matter fiber extrusion and partial arrangement materials have recently been developed, opening up new possibilities for chemical doping modification [2].

Yuan Xu and Xin Li proposed and studied a composite support substance for the catalyst. A small number of single-walled carbon nanotubes (SWNTS) were prepared, characterized and studied by cyclic voltammetry for methanol electrooxidation. Compared with the control (undoped SWCNTs), a moderate amount of SWCNT-doped catalyst was five times more active, and the addition of carbon nanotubes (SWCNTs) to the commercial carbon surface reaction zone was catalytic for methanol oxidation. A remedy is offered by this hybrid catalyst support matrix for PtRu electrocatalysts lacking (CB) loading. SWCNTs doped pure CB spheres into SWCNT-CB hybrid matrix, which altered the distribution of PtRu nanoparticles to a large degree, the morphology of catalyst film, and then affected the methanol oxidation activity of the catalyst. Appropriate proportions of SWCNTs attract PtRu to surrounding SWCNTs without causing aggregation, which improves the efficiency of methanol

oxidation with equal amounts of PtRu. The effects of SWCNTs with different doping concentrations on the catalyst film were observed by scanning and transmission electron microscopy. The results show that the addition of SWCNT to PtRu/CB changes the catalyst and supports the difficulties of dispersion and accessibility of the loose type catalyst, which is a very promising catalyst system with high efficiency and economy [3].

Phase transition and staging of doped single-walled carbon nanotubes (SWNTs) is a controversial issue. N. Bendiab, L. Spina, A. Zahab et al. reported rubidium doped SWNT combined with measurements of in-situ conductivity and Raman. The significant correlation peak between the primary Raman frequency, the resistance, and how the resistance changes when exposed to laser light. Two distinct Raman signatures with peaks of 1596 and 1555 cm^{-1} were found in the final doping step and connected to two distinct stable doping phases. Within a certain doping range, the two phases coexist, with the later increasingly advancing at the expense of the former. Claye et al. recently proposed a two-phase model for alkali metal-doped SWNT using electrochemical methods, in which the doped amorphous region grows at the cost of the unadorned crystal region. The model points that spectrum of the two coexist during Raman experiments, but this co-existence has not been observed in previous studies. In this experiment, N. Bendiab et al. did observe a coexistence phase of the two substances, but their interpretation differed from Ref. 12. The undoped crystal phase, which had two primary Raman peaks near 1563 and 1592 cm^{-1} , progressively vanished in the first stage of doping, while the first doped phase (phase I), which had a single Raman peak near 1596 cm^{-1} , steadily rose up. The saturated doped phase (phase II), which grows at the expense of phase I in the final doping step, coexists with phase I within a particular doping range. N. Phases I and II's intrinsic Raman responses were given the spectra (d) and (e), respectively, by Bendiab et al. To fully evaluate the Raman/conductivity findings, structural studies will be required [4].

For both direct vapor/liquid techniques and electrochemical doping, charge-transfer doping that is reversible that creates a metallic condition for large SWNT is well known. Samples in bulk and individual ropes can show up to 40-fold increases in conductivity at 300 K, which is similar to GICs but less significant to fullerenes or conjugated polymers. The benefits of electrochemical approaches for researching fundamental physics are countered by solvent effects, which obfuscate how doping and dedoping operate, damage crystallinity, and sometimes limit the maximum dopant concentration. The predicted dilatation of the 2D rope lattice is visible in X-ray diffraction on materials with vapor doping, but the intensity profiles fall far short of fully explaining the weight uptake. As a result, it appears that all doped SWNTs have some level of disorder. As more advanced materials become accessible, this could alter. It is possible to create all-nanotube fibers by extruding a suspension into a liquid through an aperture and then drying it. This would have to be done to try increasing their conductivity via intercalation if this technique could be perfected to produce long, high-strength fibers made of well-aligned SWNT. As prospective anode materials for Li-ion batteries, Li-intercalated nanotubes are still receiving a lot of research. Using SWNT materials that have been treated to enable access to the tube's internal volume, Li capacities that are greater than twice as much as those of graphite have been reported. The excessively large irreversible capacity caused by external parasite reactions (which is made worse in these very permeable substances), charge and discharge with a significant hysteresis, and a large difference between the anode potential and the Li/Li⁺ ranging from completely charged to fully discharged are some of the major problems that still need to be solved.

Earlier claims that intercropping tubes with alkaline metal would increase the capacity of hydrogen storage has now been disproved as an experimental artifact. A quantum dot or a single-electron transistor, is created when a semiconducting SWNT with a 200–500 nm length is exposed to K vapor. This quantum dot may be switched between the states of on and off by applying 2 V to the reverse-gate electrode. Targeting interstitial regions in a more or less well-defined lattice without altering the structure and internal bonds of the host motif is referred to as intercalation chemistry. It is obvious that other nanotube chemistries are feasible. Haddon and Sun's accounts in this issue cover responses affecting sidewalls and tube ends (whether open or closed). Filling the inside annulus is a different option that was mentioned earlier. Oxidation has the ability to open the ends of multiwall tubes, and

the annulus is big enough to allow capillary forces to take liquids with low surface tension in. From precursors of molten oxide or salt, solitary organic crystals can be formed inside appropriately prepared nanotubes. By initially etching holes into the sidewalls, the abundance of C₆₀, higher fullerenes, and endofullerenes in SWNT is possible. It would be crucial to include functional molecules of biological importance in rational tube filling synthesis.

The hydrogen fuel would be practical for the creation of clean energy if it were to be made of materials that are light-weight and large focused areas that could contain a lot of hydrogen. Adsorbing different carbonaceous materials with hydrogen, including carbon nanotubes, carbon-derived compounds, and activated carbon, is one of the areas that is now being actively researched (CNTs). The original carbon nanotubes are widely acknowledged to be unsuitable for storing hydrogen materials (adsorption of hydrogen less than 1%). Additionally, atomic adsorption has high energy stability, making it less than ideal as a storage mechanism. In order to improve storage applications, some scientists have been concentrating on ways to boost molecular adsorption energy or decrease atomic adsorption energy. This is due to the possibility that functionalizing CNTs with transition metal elements may allow them to store substantial amounts of hydrogen through the TM-d states and the H₂ states interchanging, which have binding energies ranging from 0.2e to 0.6eV. For a thorough investigation of the electrical structure and morphological traits of uncoated and single-walled CNTs that are co-doped with exo-hydrogen, density functional theory (DFT) simulations using the approximate generalized gradient method (GGA) were used. Investigations were conducted on three cobalt adatoms' doping configurations: two inside and one outside. The binding energies, bond lengths, and angles under full and half concentration of the adsorbed hydrogen atoms were calculated for both conditions. Exo-hydrogenated CNTs with full and half coverage conditions would be stable in the internally doped Co atom systems, even if the stability of the hydrogenated systems under externally doped Co adatom was unclear. This was demonstrated by the outcome of the Co-3d and H-s orbitals' hybridization. In general, the amount of total hydrogens adsorbed can vary significantly when Co is added externally, however when Co is added internally, the nanotube's chirality determines the exo-nature hydrogenation's (atomic or molecular) [5].

2.2 Multi-walled carbon nanotubes

The wall of a multi-walled tube is typically covered in tiny holes that resemble flaws because it is simple to become the trap center between layers during the early stages of multi-walled tube creation. The diameter of a multi-walled tube can range from 2 to 100 nanometers, with the innermost layer of the tube being as thin as 0.4 nanometers.

Using X-ray photoemission spectroscopy (XPS) and transmission electron microscopy, Jun Hyung Lim et al. examined the impact of nitrogen doping on the structure and crystallinity of multi-walled carbon nanotubes that resemble bamboo (BS-MWNTs) (TEM). During chemical vapor deposition, the nitrogen concentration can be adjusted from 0.4% to 2.4% by adjusting the NH₃/C₂H₂ flow ratio. According to XPS, when the level of nitrogen rises, N-SP³ carbon bonds grow and crystallinity declines. Additionally, above 5% nitrogen concentration, N-SP³ carbon bonds were much more prevalent than N-SP² carbon bonds. Shorter spacing distances are seen in BS-CNTs at greater nitrogen concentrations, which may be a result of the suppression of carbon diffusion on the catalyst particles' surfaces [6].

Based on density functional theory, XIAO Yang et al. investigated the co-doping of potassium and bromine in SWNTs and TWNTs. When potassium's 4s electrons are transported to nanotubes and bromine in co-doped (6,0)SWCNTs, the result is the n-type properties of SWCNTs. The outer and inner tubes of the (7,0)@(16,0)DWCNT have positive and negative charges, respectively, when potassium is placed into the inner tube and bromine is inserted into the outer tube. It is anticipated that DWCNTs will make the best P-N junction and diode candidates [7].

2.3 Other types of carbon nanotubes

The atomic characteristics of both materials determine whether material is suitable as a doping material for a semiconductor material. Generally speaking, dopants are classified as donors and acceptors according to the charge they bring to the doped material. Most of the valence electrons brought by the donor atoms will form covalent bonds with the doped material atoms, and then be bound. Donor electron refers to an electron that is weakly bound by the donor atom and does not make a covalent link with an atom of the doped substance. The donor electrons require less energy to transition to the conduction band than the valence electrons of the intrinsic semiconductor, and they flow across the semiconductor material's lattice comparatively easily, producing an electric current. The donor atom will only be fixed in the semiconductor material's lattice after the donor electron is lost, even though the electron obtains energy and leaps to the conduction band without leaving an electric hole like the fundamental semiconductor does. An N-type semiconductor, where N stands for negatively charged electrons, is a semiconductor that receives more electrons for conduction as a result of doping. In contrast to the donor, the acceptor atom will introduce an additional vacancy when it enters the semiconductor lattice because it has less valence electrons than the semiconductor atom. This additional vacancy can be thought of as an electric hole. P-type semiconductor, where P stands for positively charged hole, is the term used to describe the acceptor doped semiconductor. An intrinsic silicon semiconductor is used to demonstrate how doping works. Silicon contains four valence electrons and is frequently added to trivalent and pentavalent element complexes as a dopant. Boron serves as the acceptor when it is doped into a silicon semiconductor, turning the silicon semiconductor into a P-type semiconductor. Boron is a trivalent element with only three valence electrons. Contrarily, when a pentavalent element like phosphorus is doped into a silicon semiconductor, it acts as a donor and the silicon semiconductor transformed into an N-type semiconductor.

However, not all doping will be effective, because there will be some failures in the doping of silicon with phosphorus and boron, which will not form a quadrivalent bond, but a trivalent bond, which will still not conduct electricity and will not have a PN section. High temperature thermal diffusion was used to incorporate borons into semiconducting (S) and metallic (M) SWCNT assemblies, and the thermal treatment temperature was used to modify the boron atom concentration. There are both favorable and unfavorable impacts on the incorporation of boron, depending on the conduction technique utilized in the assembly of the SWCNTs. After adding a tiny number of boron atoms, the S-SWCNT plate's resistivity drops by around one order as a result of the local condition of hopping conduction. On the other hand, we noticed a rise in the resistivity of boron-doped M-SWCNTs. When an external magnetic field perpendicular to the film is applied, the resistivity of the original and boron-doped metal SWCNTs decreases, which points to a two-dimensional weak localization characteristic. The increased inelastic scattering events at boron-doped sites shorten the phase coherence length, which causes the resistivity to increase, based on a careful analysis of resistivity and magnetoresistance.

Yu Zhang et al. synthesized nitrogen doped iron particle carbon nanotubes (NCNTs/Fe) for microwave absorption using a basic technique. It is practical for mass manufacturing. Without any pretreatment, the produced sample can be simply spread into the matrix. Iron particles of micron to nanometer size were observed in 50 ~ 500 nm diameter shells and bamboo-like nanotubes. By using X-ray diffraction and Mossbauer spectroscopy, the Fe phase structure of NCNTs/Fe was investigated. It primarily contained Fe and Fe₃. Different mass ratios of carbon nanotubes and paraffin composites were investigated for their electromagnetic characteristics. It's interesting to note that the substance exhibits good microwave absorption capabilities, with a reflection loss (RL) of 1.58 mM NCNTs/Fe combined with paraffin (20% mass ratio) reaching 57.96 dB at 14.96 GHz bandwidth (RL10 dB) of 3.52 GHz [8].

Bon-doped carbon nanotubes may make up an appropriate class of materials for nanoelectronic technology because it is projected that they will behave as semiconductors over a wide range of diameters and chirality. For instance, they can be utilized to improve the capacitance and charging and discharging times of supercapacitors. This work proposes a new method for producing boron-

doped carbon nanotubes through electric arc, using boron as a doping element and nickel and yttrium as catalysts. With this method, carbon nanotubes may be produced with an 8% boron dope in a short period of time (2 minutes) and with minimal power input (2 kW). Scanning and transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy were used to analyze boron doped carbon nanotubes. Emission spectroscopy is used to examine the physical aspects of plasma. It is good for synthesis since the temperature around 5000 K suggests a high concentration of C₂ molecules [9].

Purification and Structure and Electrical Properties of KAuBr₄(AQ) -doped hemicrystalline SWCNT thin films were irradiated with 150-KeV 11B⁺ ions to introduce defects in the range of $1 \times 10^{12} \sim 1 \times 10^{15}$ ions /cm². Before irradiation, the conductivity of doped S-SWNTs and M-SWNTs was increased by 20× and 2×, respectively. With increasing defect density, irradiation of the sample resulted in a decrease in the conductivity of both purified and doped electron types of SWCNTs. However, the chemical dopant's relative conductivity improvement is kept, leading to a more radiation-resistant electrical conductor. Dopants do not change the degree of SWCNT damage, but instead alter the electrical characteristics of SWCNTs by raising the carrier concentration [10].

3. Conclusions

This paper first introduces the properties of carbon nanotubes and emphasizes the characteristics when compared with other traditional materials in some specific fields. Physical properties of the material have been enhanced with the help of CNTs, so carbon nanotubes have a wide range of application prospects in many fields. In this paper, the performance of carbon nanotubes can be further enhanced by the incorporation of some trace impurities through the review of previous literature. For example, SWNTS can be doped or inserted into electron donors or acceptors to enhance their electrical conductivity, as well as obtaining conductive electron paramagnetism, reversibility in part or fully and cyclicity. Functionalized carbon nanotubes with transition metal elements, through the TM-D and H₂ states interchanging states, could potentially allow them to store large amounts of hydrogen, with 0.2~0.6 eV binding energies, among other examples. Therefore, doping is an indispensable means to apply carbon nanotubes in various fields in the future. It is suggested that if conditions permit, people can try to doping various trace impurities in carbon nanotubes, so as to obtain some new methods to change their properties, which is of great significance in various disciplines such as physics, biology and even environmental science. As mentioned in this paper, these conclusions are drawn by summarizing the previous literature, and are not well proved by experiments. In the future, more experiments can be done to make up for the lack of experiments in this paper and optimize the operational details for further research on this topic.

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