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CARBON NANOTUBES: AN APPROACH TO NOVEL DRUG DELIVERY SYSTEM

M. H. Alai*, S. P. Poptani and G.V. Patil

Department of Pharmaceutics, Rajarambapu College of Pharmacy, Kasegaon- 415404, Maharashtra, India

ABSTRACT

Keywords: Arc discharge method, Carbon Nanotube, Laser ablation method, Multiwalled nanotube

Correspondence to Author:

Manoj Hari Alai

Radhai Niwas, Behind bus stand, A/P-Nampur, Tal- Satana, Dist- Nasik- 423204, Maharashtra, India Carbon nanotubes are cylindrical carbon molecules have novel properties, making them potentially useful in many applications in nanotechnology, electronics, optics, and other fields of material science as well as potential uses in architectural fields. They have unique electronic, mechanical, optical and chemical properties that make them good candidates for a wide variety of applications, including drug transporters, new therapeutics, delivery systems and diagnostics. Their unique surface area, stiffness, strength and resilience have led to much excitement in the field of pharmacy. Nanotubes are categorized as single-walled nanotubes, multiple walled nanotubes. Various techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, chemical vapor deposition. They can pass through membranes, carrying therapeutic drugs, vaccines and nucleic acids deep into the cell to targets previously unreachable. Purification of the tubes can be divided into a couple of main techniques: oxidation, acid treatment, annealing, sonication, filtering and functionalization techniques. The main problem of insolubility in aqueous media has been solved by developing a synthetic protocol that allows highly water-soluble carbon NTs to be obtained. The modifications are done to improve efficiency of carbon nanotubes by formulating luminescent carbon nanotubes, ultrathin carbon nanoneedles, magnetically guided nanotubes. The application of carbon nanotube in tissue engineering, drug carrier release system, wound healing, in cancer treatment and as biosensor. Researchers have recently developed a new approach to Boron Neutron Capture Therapy in the treatment of cancer using substituted Carborane-Appended Water-Soluble single-wall carbon nanotubes.

INTRODUCTION: Carbon nanotubes (CNTs; also known as buckytubes), not to be confused with Carbon Fiber, are allotropes of carbon with a cylindrical nanostructure.

Nanotubes have been constructed with length-todiameter ratio of up to 132,000,000:1, significantly larger than any other material. These cylindrical carbon molecules have novel properties, making them potentially useful applications in many in nanotechnology, electronics, optics, and other fields of materials science, as well as potential uses in architectural fields. They may also have applications in the construction of body armor. They exhibit extraordinary strength and unique electrical properties, and are efficient thermal conductors ¹.



FIG. 1: TYPICAL STRUCTURE OF CARBON NANOTUBE.

Nanotubes are members of the fullerene structural family, which also includes the spherical buckyballs. The ends of a nanotube may be capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 1/50,000th of the width of a human hair), while they can be up to 18 centimeters in length (as of 2010). Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs)¹.



FIGURE 2: CARBON FILAMENT

A 6 μ m diameter carbon filament (running from bottom left to top right) compared to a human hair. Each carbon filament thread is a bundle of many thousand carbon filaments. A single such filament is a thin tube with a diameter of 5-8 micrometers and consists almost exclusively of carbon. The earliest generation of carbon fibers (i.e., T300, and AS4) had diameters of 7-8 micrometers. Later fibers (i.e., IM6) have diameters that are approximately 5 micrometers ^{2, 3}.

Discovery: In 1952, L. V. Radushkevich and V. M. Lukyanovich published clear images of 50 nanometer diameter tubes made of carbon in the Soviet *Journal of Physical Chemistry*. This discovery was largely unnoticed, as the article was published in the Russian language, and Western scientists' access to Soviet press was limited during the Cold War.

In 1979, John Abrahamson presented evidence of carbon nanotubes at the 14th Biennial Conference of Carbon at Pennsylvania State University. The conference paper described carbon nanotubes as carbon fibers which were produced on carbon anodes during arc discharge. A characterization of these fibers was given as well as hypotheses for their growth in a nitrogen atmosphere at low pressures. In 1981 a group of Soviet scientists published the results of chemical and structural characterization of carbon nanoparticles produced by a thermocatalytical disproportionation of carbon monoxide. Using TEM images and XRD patterns, the authors suggested that their "carbon multi-layer tubular crystals" were formed by rolling graphene layers into cylinders. They speculated that by rolling graphene layers into a cylinder, many different arrangements of graphene hexagonal nets are possible. They suggested two possibilities of such arrangements: circular arrangement (armchair nanotube) and a spiral, helical arrangement (chiral tube).

In 1987, Howard G. Tennett of Hyperion Catalysis was issued a U.S. patent for the production of "cylindrical discrete carbon fibrils" with a "constant diameter between about 3.5 and about 70 nanometers..., length 10^2 times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core ⁴.

lijima's discovery of multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods in 1991 and Mintmire, Dunlap, and White's independent prediction that if single-walled carbon nanotubes could be made, then they would exhibit remarkable conducting properties helped create the initial buzz that is now associated with carbon nanotubes. Nanotube research accelerated greatly following the independent discoveries by Bethune at IBM and lijima at NEC of *single-walled* carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge.

The arc discharge technique was well-known to produce the famed Buckminster fullerene on a preparative scale, and these results appeared to extend the run of accidental discoveries relating to fullerenes. The original observation of fullerenes in mass spectrometry was not anticipated, and the first mass-production technique by Krätschmer and Huffman was used for several years before realizing that it produced fullerenes ⁵.

Allotropes of Carbon ⁶:

Diamond: Diamond is one of the best known allotropes of carbon. The hardness and high dispersion of light of diamond make it useful for both industrial applications and jewellery. Diamond is the hardest known natural mineral. This makes it an excellent abrasive and makes it hold polish and luster extremely well. No known naturally occurring substance can cut (or even scratch) a diamond.



FIG. 3 : SOME ALLOTROPES OF CARBON: A) DIAMOND; B) GRAPHITE; C) LONSDALEITE; D–F) FULLERENES (C_{60} , C_{540} , C_{70}); G) AMORPHOUS CARBON; H) CARBON NANOTUBE.

Graphite: (named by Abraham Gottlob Werner in 1789, from the Greek γράφειν (*graphein*, "to draw/write", for its use in pencils) is one of the most common allotropes of carbon. Unlike diamond, graphite is an electrical conductor. Thus, it can be used in, for instance, electrical arc lamp electrodes. Likewise, under standard conditions, graphite is the most stable form of carbon. Therefore, it is used in thermochemistry as the standard state for defining the heat of formation of carbon compounds.

Graphite conducts electricity, due to delocalization of the pi bond electrons above and below the planes of the carbon atoms. These electrons are free to move, so are able to conduct electricity. However, the electricity is only conducted along the plane of the layers. In diamond, all four outer electrons of each carbon atom are 'localized' between the atoms in covalent bonding. The movement of electrons is restricted and diamond does not conduct an electric current.

In graphite, each carbon atom uses only 3 of its 4 outer energy level electrons in covalently bonding to three other carbon atoms in a plane. Each carbon atom contributes one electron to a delocalized system of electrons that is also a part of the chemical bonding. The delocalized electrons are free to move throughout the plane. For this reason, graphite conducts electricity along the planes of carbon atoms, but does not conduct in a direction at right angles to the plane.

Carbon nanofoam: Carbon nanofoam is the fifth known allotrope of carbon discovered in 1997 by Andrei V. Rode and co-workers at the Australian National University in Canberra. It consists of a low-density cluster-assembly of carbon atoms strung together in a loose three-dimensional web.

The large-scale structure of carbon nanofoam is similar to that of anaerogel, but with 1% of the density of previously produced carbon aerogels - only a few times the density of air at sea level. Unlike carbon aerogels, carbon nanofoam is a poor electrical conductor.

Geometry of CNTS⁷:

- Three unique geometries of CNTs can be possible
- The three different geometries are also referred to as *flavors*



FIG. 4: ARMCHAIR ARRANGEMENT



FIG. 5: ZIG-ZAG ARRANGEMENT



FIG. 6: CHIRAL ARRANGEMENT

Types of carbon nanotubes and related structures:

Single-walled: Single-walled nanotubes are an important variety of carbon nanotube because they exhibit electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior, whereas MWNTs are zero-gap metals. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors. One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FET).



FIG. 7: SINGLE-WALLED TYPES OF CARBON NANOTUBES

Single-walled nanotubes are dropping precipitously in price, from around \$1500 per gram as of 2000 to retail prices of around \$50 per gram of as-produced 40–60% by weight SWNTs as of March 2010

Multi-walled: Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphite. There are two models which can be used to describe the structures of multi-walled nanotubes. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, e.g. a single-walled nanotube (SWNT) within a larger (0, 17) single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å.



FIG. 8: TRIPLE-WALLED ARMCHAIR CARBON NANOTUBE

Properties of CNT:

Strength ^{8, 9, 10}: Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp² bonds formed between the individual carbon atoms. In 2000, a multiwalled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa). (This, for illustration, translates into the ability to endure tension of a weight equivalent to 6422 kg on a cable with cross-section of 1 mm².) Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g·cm⁻³, its specific strength of up to 48,000 kN·m·kg⁻¹ is the best of known materials, compared to high-carbon steel's 154 kN·m·kg⁻¹.

Hardness ¹¹: Standard single walled carbon nanotubes can withstand a pressure up to 24GPa without deformation. They then undergo a transformation to superhard phase nanotubes. Maximum pressures measured using current experimental techniques are around 55GPa. However, these new superhard phase nanotubes collapse at an even higher, albeit unknown, pressure. The bulk modulus of superhard phase nanotubes is 462 to 546 GPa, even higher than that of diamond (420 GPa for single diamond crystal). **Electrical**^{12, 13, 14}: Band structures computed using tight binding approximation for (6, 0) CNT (zigzag, metallic) (10, 2) CNT (semiconducting) and (10, 10) CNT (armchair, metallic).

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n, m) nanotube, if n = m, the nanotube is metallic; if n - m is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair (n = m) nanotubes are metallic, and nanotubes etc. are semiconducting.

Thermal ^{15, 16, 17}: All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal

TABLE 1: METHOD AND SPECIFICATIONS

conductivity along its axis of about 3500 W·m⁻¹·K⁻¹; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 W·m⁻¹·K⁻¹. A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 W·m⁻¹·K⁻¹, which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to 2800°C in vacuum and about 750°C in air.

Synthesis of Carbon Nanotube: Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

Method	Arc discharge method	Chemical vapor deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms hot plasma.	Place substrate in oven, heat to 600 oC, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100%	Upto 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approx 10 nm	Long tubes with diameter ranging from 10-240 nm	it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

1. Arc Discharge Method ^{18, 19}: Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps that was intended to produce fullerenes. However the first macroscopic production of carbon nanotubes

was made in 1992 by two researchers at NEC's Fundamental Research Laboratory. The method used was the same as in 1991. During this process, the carbon contained in the negative electrode sublimates because of the high discharge temperatures. Because nanotubes were initially discovered using this technique, it has been the most widely-used method of nanotube synthesis.



FIG. 9: ARC DISCHARGE METHOD

2. Laser Ablation Method ^{20, 21}: In the laser ablation process, a pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. This process was developed by Dr. Richard Smalley and coworkers at Rice University, who at the time of the discovery of carbon nanotubes, were blasting metals with a laser to produce various metal molecules. When they heard of the existence of nanotubes they replaced the metals with graphite to create multi-walled carbon nanotubes.

Later that year the team used a composite of graphite and metal catalyst particles (the best yield was from a cobalt and nickel mixture) to synthesize single-walled carbon nanotubes. The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.



FIG. 10: LASER ABLATION METHOD

3. Chemical Vapor Deposition (CVD) ^{22, 23}: The catalytic vapor phase deposition of carbon was first reported in 1959, but it was not until 1993 that carbon nanotubes were formed by this process. In 2007, researchers at the University of Cincinnati (UC) developed a process to grow aligned carbon nanotube arrays of 18 mm length on a FirstNano ET3000 carbon nanotube growth system. During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination. The metal nanoparticles can also be produced by other ways, including reduction of oxides or oxides solid solutions.

The diameters of the nanotubes that are to be grown are related to the size of the metal particles. This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The substrate is heated to approximately 700°C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen or hydrogen) and a carboncontaining gas (such as acetylene, ethylene, ethanol or methane).

Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This mechanism is still being studied.

The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate. Thermal catalytic decomposition of hydrocarbon has become an active area of research and can be a promising route for the bulk production of CNTs. Fluidized bed reactor is the most widely used reactor for CNT preparation. Scale-up of the reactor is the major challenge.



FIG. 11: CHEMICAL VAPOR DEPOSITION METHOD

4. CoMoCat process ²⁴: In this method, SWNTs are grown by CO disproportionation at 700 – 950°C. The technique is based on a unique Co-Mo catalyst formulation that inhibits the sintering of Co particles and therefore inhibits the formation of undesired forms of carbon that lower the selectivity. During the SWNT reaction, cobalt is progressively reduced from the oxidic state to the metallic form.

Simultaneously Molybdenum is converted to the carbidic form (Mo₂C). Co acts as the active species in the activation of CO, while the role of the Mo is possibly dual. It would stabilise Co as a well-dispersed Co^{2+} avoiding its reduction and would act as a carbon sink to moderate the growth of carbon inhibiting the formation of undesirable forms of carbon44.



FIG. 12: SHOWS A FLUIDISED BED REACTOR FOR A COMOCAT PROCESS

Purification of Carbon Nanotubes ^{25, 26, 27}: A large problem with nanotube application is next to largescale synthesis also the purification. The purification of SWNTs will be discussed. The as-produced SWNT soot contains a lot of impurities. The main impurities in the soot are graphite (wrapped up) sheets, amorphous carbon, metal catalyst and the smaller fullerenes. These impurities will interfere with most of the desired properties of the SWNTs. Also in the fundamental research, it is preferred to obtain SWNTs or the impurities, as pure as possible without changing them. In order to understand the measurements better, the SWNT samples also have to be as homogeneous as possible. The common industrial techniques use strong oxidation and acid refluxing techniques, which have an effect on the structure of the tubes.

- Oxidation
- Acid treatment
- Annealing
- Ultrasonication
- Magnetic Purification
- Functionalization
- Cutting
- Micro filtration

Toxicity Aspects ²⁸: Determining the toxicity of carbon nanotubes has been one of the most pressing questions in nanotechnology. Unfortunately, such research has only just begun. Thus, the data are still fragmentary and subject to criticism.

Preliminary results highlight the difficulties in evaluating the toxicity of this heterogeneous material. Parameters such as structure, size distribution, surface area, surface chemistry, surface charge, and agglomeration state as well as purity of the samples, have considerable impact on the reactivity of carbon nanotubes. However, available data clearly show that, under some conditions, nanotubes can cross membrane barriers, which suggests that if raw materials reach the organs they can induce harmful effects such as inflammatory and fibrotic reactions.

FunctionalizationofCarbonNanotube:Functionalization is based on making SWNTs more
soluble than the impurities by attaching other groups
to the tubes. Now it is easy to separate them from
insoluble impurities, such as metal, with filtration.

Another Functionalization technique also leaves the SWNT structure intact and makes them soluble for chromatographic size separation.

For recovery of the purified SWNTs, the functional groups can be simply removed by thermal treatment, such as annealing.







Side-wall Functionalization:



Characterization of CNTS: ²⁹

- 1. Photoluminescence spectroscopy: Photoluminescence is arises as a recombination of electron hole pair at band gap. Gap energy of the semiconducting tubes is related to the chirality. Determination of photoluminescence is carried out in the unbundled CNTs.
- 2. X-ray photoelectron spectroscopy (XPS): This implies chemical interaction with organic compounds or gas absorption, and depends on the chemical structure of carbon nanotubes; also chemical functionalization can be judged.
- Scanning tunneling microscopy (STM): CNTs must be deposited on flat conducting surface like HOPG or Au for this study and to get the 3-D morphology of tubes (correlated with SEM). Also simultaneous determination of atomic structure and electronic density of state (DOS)
- 4. **Neutron diffraction**: Neutron diffraction pattern can be affected by various factors like finite size of nanotubes bundles, number of tubes in bundles, and nanotubes diameters polydispersivity. Determination of structural

features such as bond length and possible distortion of hexagonal network is possible by using this method. For smallest diameters; CNTs a distinction between *armchair, zigzag and chiral nanotubes* can be achieved.

- 5. X-ray diffraction (XRD): XRD pattern of CNTs is close to graphite; multiple orientations of CNTs can be possible according to X-ray incident beam, Information on the interlayer spacing, the structural strain and the impurities and are also observed as well as various numbers of layers for MWNTs
- Transmission electronic microscopy (TEM): Length and diameter of CNTs can be determined by TEM, Changes in physical and chemical properties by change in intershell spacing which gives difference in transmission.
- Infrared spectroscopy (IR): IR spectroscopy is used to determine impurities remaining from synthesis or molecules capped on the nanotube surface. Infrared active modes are present in SWCNTs depending on the symmetry: *chiral*, *zigzag and armchair*, *For MWCNTs these are observed at* 868 cm⁻¹ and 1575 cm⁻¹

Applications: ^{30, 31}

Various applications of CNTs are as follows:

- 1. In technological Applications; Energy storage like Hydrogen storage, Lithium intercalation, electrochemical supercapacitors. Also some Nanoprobes and sensors which mostly involves Transistors and Ultra capacitors.
- Biomedical Applications suggests that the carbon nanotubes are suitable scaffold materials for osteoblast proliferation and bone formation.
- 3. Cisplatin incorporated oxidized SWNHs have showed slow release of Cisplatin in aqueous environment. The released Cisplatin had been effective in terminating the growth of human lung cancer cells, while the SWNHs alone did not show anticancer activity.
- Anticancer drug Polyphosphazene platinum givenwith nanotubes had enhanced permeability, distribution and retention in the brain due to controlled lipophilicity of nanotubes.
- 5. They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with vander waals forces.
- Carrier for Drug delivery: Carbon nanohorns (CNHs) are the spherical aggregates of CNTs with irregular horn like shape. Research studies have proved CNTs and CNHs as a potential carrier for drug delivery system.
- 7. Functionalized carbon nanotubes are reported for targeting of Amphotericin B to Cells.
- Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration.
- Structural Applications includes tennis rackets, bicycle parts, golf balls, golf clubs, and baseball bats, also Ideal for synthetic muscle.

10. CNTs act as Biosensors for the detection of Glucose and DNA.

Recent Advancement:

- Carbon nanotubes (CNTs) are very prevalent in today's world of medical research and are being highly researched in the fields of efficient drug delivery and biosensing methods for disease treatment and health monitoring. Carbon nanotube technology has shown to have the potential to alter drug delivery and biosensing methods for the better, and thus, carbon nanotubes have recently garnered interest in the field of medicine.
- 32. Boron Neutron Capture Therapy Researchers have recently developed a new approach to Boron Neutron Capture Therapy in the treatment of cancer using substituted Carborane-Appended Water-Soluble single-wall nanotubes. Substituted carbon C2B10 carborane cages were successfully attached to the side walls of single wall carbon nanotubes (SWCNTs) via nitrene cycloaddition. The decapitations of these C2B10 carborane cages, with the appended SWCNTs intact, were accomplished by the reaction with sodium hydroxide in refluxing ethanol. During base reflux, the three-membered ring formed by the nitrene and SWCNT was opened to produce water-soluble SWCNTs in which the side walls were functionalized by both substituted nido-C2B9 carborane units and ethoxide moieties.

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