

METHOD FOR DISPERSING CARBON NANOTUBES USING CHONDROITIN SULFATE CATION SALT

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of United States Provisional Patent Application No. 61/383,905, filed 17 September 2010, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The invention relates to a method of dispersing carbon nanotubes, and in particular, to a method of dispersing single-walled carbon nanotubes using chondroitin sulfate.

Background

[0003] Single-walled carbon nanotubes (SWNTs) possess excellent mechanical, optical and electrical properties, and have been proposed for use in a wide range of applications. However, as-produced SWNTs are aggregated due to strong van der Waals interactions between individual tubes.

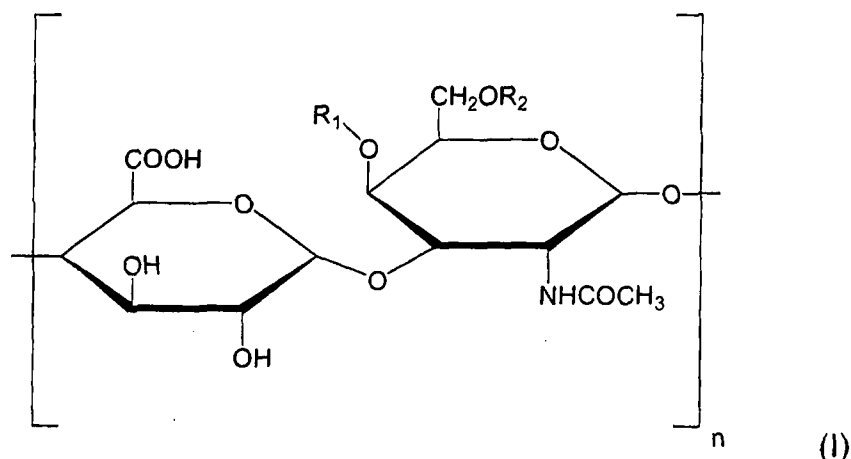
[0004] Furthermore, as-produced SWNTs typically consist of mixtures of metallic and semiconducting species with different diameters and chiral angles. Their poor solubility in water and the presence of metallic tubes hinder to a certain extent their use in applications such as field effect transistors (FETs).

[0005] Therefore, there is a need to reduce aggregation and to disperse the carbon nanotubes as individual tubes.

Summary

[0006] According to one aspect, there is provided a method for dispersing carbon nanotubes. The method includes:

(a) providing a solution containing chondroitin sulfate cation salt of formula (I)



wherein

R_1 is MSO_3 and R_2 is H, or R_1 is H and R_2 is MSO_3 ;

M is an alkaline metal, or an alkaline earth metal further bound to a monovalent counter-anion;

n is at least 20; and

(b) contacting the carbon nanotubes with the solution containing the chondroitin sulfate cation salt.

[0007] In another aspect, the invention relates to the use of a chondroitin sulfate cation salt of formula (I) for dispersing carbon nanotubes.

[0008] A further aspect relates to a chondroitin sulfate cation salt of formula (I) for use as a dispersant for carbon nanotubes.

[0009] In yet another aspect, a carbon nanotube having the present chondroitin sulfate cation salt of formula (I) attached thereto is provided.

Brief Description of the Drawings

[0010] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0011] **Fig. 1** shows isomers of chondroitin sulfate (CS) (a) CS-A (b) CS-B, and (c) CS-C.

[0012] **Fig. 2** shows the CD spectra of the three isomers CS-A, CS-B, and CS-C.

[0013] **Fig. 3** shows the deconvolution results of CD spectra with CDNN software.

[0014] **Fig. 4** shows (A) UV-vis-NIR results, (B) $A(S)/A(T)$ ratio, and (C) absorbance at 500nm of the three isomers CS-A, CS-B, and CS-C. The straight line of each graph is a linear-least-squares fitted to the data.

[0015] **Fig. 5** shows (A) UV-vis-NIR result of PVP as dispersant of HiPco SWNTs in aqueous solution, (B) absorbance at 500nm, as comparative example. The straight line of each graph is a linear-least-squares fitted to the data.

[0016] **Fig. 6** shows (a) photoluminescence results; (b) relative abundance graphene maps for SDS/(HiPco SWNT), CS-A/(HiPco SWNT), CS-B/(HiPco SWNT), and CS-C/(HiPco SWNT); (c) plots of relative abundance of each chirality of SDS/HiPco, CS-A/HiPco, CS-B/HiPco and CS-C/HiPco; (d) emission peaks of different HiPco solutions. Emission peaks red-shifted from CS-B/HiPco SWNT solution for CS-A/HiPco and CS-C/HiPco SWNT solution.

[0017] Fig. 7 shows computer simulated conformations of the heptamer isomers: (a) CS-A, (b) CS-B, and (c) CS-C, in water.

[0018] Fig. 8 shows intramolecular interactions of (a) CS-A, (b) CS-B, and (c) CS-C monomers (Left: computer model; Right: the illustrations). The dotted lines show the interaction in the monomer.

[0019] Fig. 9 shows computer simulation structure models of CS-SWNT (7,6) complex, specifically (7,6) SWNT with (a) CS-A, (b) CS-B, and (c) CS-C wrapping around the SWNT, (d) schematic of CS wrapping around a nanotube.

[0020] Fig. 10 shows (A) XPS results of HiPco SWNT solutions with SDS and CS-A, and (B) the binding energies of different CS-SWNT complexes estimated by GB model.

[0021] Fig. 11 shows the binding energy between polymer and SWNTs with different tube diameters.

[0022] Fig. 12 shows the binding energy between polymer and SWNTs with different tube chiral angle.

[0023] Fig. 13 shows Raman spectra of acid purified HiPco SWNT and CS-A/HiPco SWNT complex with (I) 633nm source laser and (II) 514nm source laser.

[0024] Fig. 14 shows (A1) TEM image of washed CS-A/(HiPco SWNT) on the carbon layer of a TEM grid; (A2) AFM image of washed CS-A/(HiPco SWNT) on Si; (B1) TEM image of washed CS-B/(HiPco SWNT) on the carbon layer of a TEM grid; (B2) AFM image of washed CS-B/(HiPco SWNT) on Si; (C1) TEM image of washed CS-C/(HiPco SWNT) on the carbon layer of a TEM grid; (C2) AFM image of washed CS-C/(HiPco SWNT) on Si; (A3, B3, C3) Enlarged AFM view of washed CS-A/HiPco, CS-B/HiPco, and CS-C/(HiPco SWNT), and height profiles along the line showing the polymer helical wrapping of the SWNT.

[0025] Fig. 15 shows SWNT network device using CS-A/CoMoCAT SWNTs. (A) A typical V_g - I_d graph (the channel width is $50\mu\text{m}$ and the length is $50\mu\text{m}$); (B) AFM image of the region between the electrodes; (C) histogram of percentage of number of devices with various on/off ratios. SDBS/CoMoCAT solution is used as the reference and the number of devices tested for CS-A/CoMoCAT and SDBS/CoMoCAT are 30 and 50, respectively.

[0026] Fig. 16 shows the relative PLE intensities of identified semiconducting species in HiPco-SWNT solutions with CS-A, CS-B and CS-C isomers.

Description

[0027] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0028] Various embodiments provide for a method for dispersing carbon nanotubes. The carbon nanotubes may be dispersed in water, for example. The carbon nanotubes may be contacted with a solution containing chondroitin sulfate cation salt (or chondroitin sulfate, for short). The chondroitin sulfate wraps around individual carbon nanotube and prevent aggregation of the carbon nanotubes.

[0029] A carbon nanotube as used in various embodiments may be a cylinder of rolled up graphitic sheets. Single-, double- and multi-walled carbon nanotubes are known. The carbon nanotubes may be of any desired length, such as in the range from about 0.1nm to about 10 μ m, such as from about 1nm to about 5 μ m or from 10nm to about 1 μ m. In various embodiments, the carbon nanotubes may have a length of at most about 2 μ m or a length in the range from about 0.5 μ m to about 2 μ m or from about 1 μ m to about 2 μ m. The conductivity of the carbon nanotubes used may be freely selected according to any specific requirements. Depending on the arrangement of the carbon hexagon rings along the surface of the nanotubes, carbon nanotubes can be metallic or semiconducting.

[0030] Carbon nanotubes exist in different forms, such as single-walled carbon nanotubes (SWNT), double-walled carbon nanotubes (DWNT), multi-walled carbon nanotubes (MWNT), or modified multi-walled carbon nanotubes. Although various embodiments described herein relate to SWNT, it is to be understood and appreciated that other forms or configurations of the carbon nanotubes may also be useful.

[0031] A SWNT is a seamless cylinder formed from one graphite layer. For example, carbon nanotubes can be described as a graphite plane (so called graphene) sheet rolled into a hollow cylindrical shape so that the structure is one-dimensional with axial symmetry, and in general exhibiting a spiral conformation, called chirality. A single-wall nanotube can be defined by a cylindrical sheet with a diameter of about 0.7 to about 20nm, such as about 1 to about 20nm.

[0032] A DWNT has two layers of graphite sheets rolled in to form a tube shape. The two layers of graphite sheets can form a concentric cylinder. The nanotubes are considered as a cross between SWNT and MWNT as they can have the electronic properties of the SWNT, and the mechanical strength of MWNT. DWNT may be semi-conducting or metallic.

[0033] A MWNT has multiple layers of graphite rolled in on to form a tube shape. The nanotubes can also exist in forms in which they have hydrophilic groups such as hydroxyl group, pyrenes, esters, thiols, amines, a carboxyl group and mixtures thereof on their surface.

[0034] Carbon nanotubes may be prepared by several different methods known in the art. For example, SWNT may be grown by carbon monoxide (CO) disproportionation (decomposition into C and CO₂) at 700-950°C in flow of pure CO at a total pressure that typically ranges from 1 to 10atm using a catalyst comprising cobalt (Co) and molybdenum (Mo) on a mesoporous silica support, leading to so-called CoMoCAT® SWNTs. Using this method, diameter control of SWNTs can be achieved. Another possibility is the synthesis using high pressure carbon monoxide (HiPco) leading to so-called HiPco SWNTs. Generally, in a HiPco method, metal catalyst is formed in situ when Fe(CO)₅ or Ni(CO)₄ is injected into a reactor along with a stream of CO gas at a temperature range of about 900-1100°C at a pressure of about 30 to 50atm. The metal catalyst formed can be in the form of nanometer sized particles. HiPco SWNTs may be produced following the disproportionation of CO by the metal catalyst particles. In various embodiments, CoMoCAT® and HiPco SWNTs were used to demonstrate the viability of the method described herein.

[0035] As-synthesized SWNTs contain mixtures of metallic and semiconducting species with different diameters and chiral angles.

Semiconducting SWNTs are known to exhibit superior field-effect behavior, for example. To minimize the effect of tube-to-tube variation on device electronic properties, networks of SWNTs, rather than individual nanotubes, have been applied in producing field effect transistors (FETs). FETs employing SWNT networks (SWNTnets) in the active channels are quite reproducible and printable, making low-cost macro-electronics possible. SWNTnet-based FETs have achieved mobilities higher than those typically achieved with semiconducting polymers. However, the presence of metallic tubes in SWNTnets impairs or destroys the switching behavior of semiconducting tubes. There exist numerous approaches to separate semiconducting SWNTs from metallic SWNTs. These strategies include the synthetic strategy of selective growth, post-synthesis solution-based separation methods (such as electrophoretic separation, dielectrophoresis, chromatography, density gradient ultracentrifugation (DGU), gel-based separation techniques, selective aromatic extraction, surfactant extraction, amine extraction, surface alignment and selective polymer wrapping) and fabrication-based techniques such as electrical breakdown of metallic nanotubes. However, many of the proposed methods do not achieve full semiconductor device yield, or do involve substantial costs.

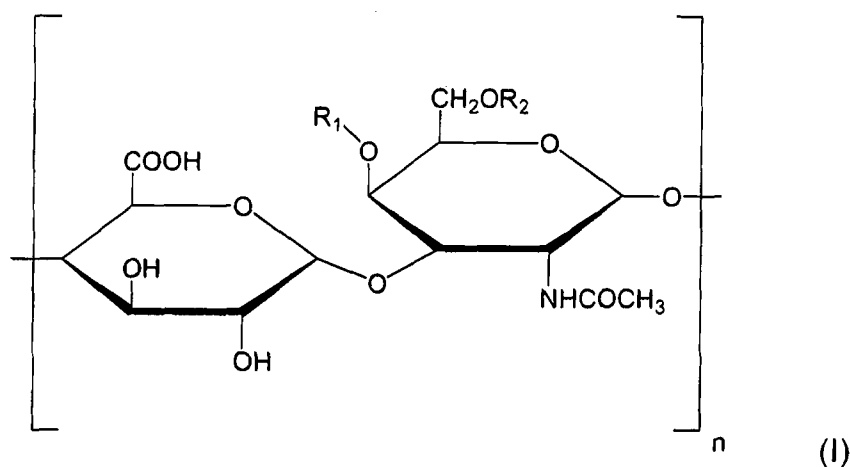
[0036] Selective functionalizations of SWNTs using small aromatic molecules which can strongly interact with SWNTs via π - π stacking interaction, have been used for selective separation of SWNTs. Such molecules include diazonium salts, pyrene derivatives, porphyrine derivatives, pentacene derivatives and flavin mononucleotide. However, most separation techniques

are still insufficient to remove metallic SWNTs to an extent sufficient to meet the requirements for electronic devices.

[0037] The present method may be used to disperse carbon nanotubes, for example SWNTs, into individual nanotubes or small bundles, instead of being in an entangled mass, prior to forming SWNTnets, and in particular SWNTnets consisting essentially of semiconducting species.

[0038] Chondroitin sulfate is a sulfated glycosaminoglycan (GAG) composed of a chain of alternating sugars (N-acetylgalactosamine and glucuronic acid). It is usually found attached to proteins as part of a proteoglycan. A chondroitin chain can have over 100 individual sugars, each of which can be sulfated in variable positions and quantities. Chondroitin sulfate thus exists in various isomeric forms. It has been found that only certain isomeric forms of chondroitin sulfate are able to effectively wrap around the nanotubes. In the present method, chondroitin sulfate cation salts existing in isomeric forms capable of forming intramolecular hydrogen bonding are useful for attaching to and thereby dispersing the carbon nanotubes. Chondroitin sulfate isomers, each having a different secondary structure, have been demonstrated (see Examples section below) to show different nanotube dispersion efficacies due to their different intramolecular interactions arising from different spatial arrangements of the functional groups. These isomers effectively disperse SWNTs into small bundles or individual tubes due to their weaker intramolecular hydrogen bonding and low amounts of alpha-helicity in their conformations (i.e. extended conformations) in solution.

[0039] In various embodiments, the chondroitin sulfate cation salt has the formula (I)



where

R_1 is MSO_3 and R_2 is H, or R_1 is H and R_2 is MSO_3 ;

M is an alkaline metal, or an alkaline earth metal further bound to a monovalent counter-anion;

n is at least 20.

[0040] In various embodiments, M may be selected from the group consisting of sodium, potassium and calcium.

[0041] In one embodiment, M is sodium.

In various embodiments, when M is an alkaline earth metal such as calcium, the monovalent counter-anion may be selected from the group consisting of chloride, bromide, iodide, chlorate, nitrate and nitrite. The divalent M is thus bound to both $-\text{SO}_3$ and the monovalent counter-anion.

[0042] In various embodiments n is 20-100,000, 20-10,000, 20-1,000, 20-500, 20-200 or 20-100.

[0043] In various embodiments, the solution of the chondroitin sulfate is an aqueous solution.

[0044] Fig. 1 shows three isomeric forms of a chondroitin sulfate sodium salt. For the discussion hereinafter, the isomer shown in Fig. 1A is denoted by

CS-A, the isomer shown in **Fig. 1B** is denoted by CS-B, and the isomer shown in **Fig. 1C** is denoted by CS-C.

[0045] In one embodiment, the chondroitin sulfate isomer may be CS-A.

[0046] In another embodiment, the chondroitin sulfate isomer may be CS-C.

[0047] Chondroitin sulfate isomers, each having a different secondary structure, have been demonstrated (see Examples section below) to show different nanotube dispersion efficacies due to their different intramolecular interactions arising from different spatial arrangements of the functional groups. Only CS-A and CS-C isomers effectively disperse SWNTs into small bundles or individual tubes due to their weaker intramolecular hydrogen bonding and low amounts of alpha-helicity in their conformations (i.e. extended conformations) in solution. CS-B isomer disperses SWNTs poorly due to its relatively stronger intramolecular Coulombic interaction and the highest amount of alpha-helicity in its conformation in solution. Free CS-A and CS-C in water (i.e. in the absence of nanotubes) form extended structures with relatively larger radii of gyration (R_g) of 1.3 and 1.4nm, respectively, while CS-B has a tighter ring-like structure with R_g of 1.0nm. Compared to CS-B, CS-A and CS-C have more extended wrapping around nanotubes so that their hydrophobic backbones can approach the graphene structure of the nanotube sidewall more closely, leading to more energetically favourable interactions with nanotubes and therefore better nanotube dispersion. AFM images show helical wrappings of CS-A and CS-C around the SWNTs. TEM images confirm the helical wrapping of CS-A around SWNT. XPS analysis and successful fabrication of FETs made from CS-A/CoMoCAT® establishes that CS-A is easily removed from SWNTs by washing with water. For applications in electronic devices such as transistors

(FETs) and logic circuits, the sorted semiconducting nanotubes should not be covered with residual dispersing chondroitin sulfate polymers or else the high intertube resistance would make the device performance inferior. For easy removability of the polymers after dispersion, the chondroitin sulfate polymers should not interact too strongly with the nanotubes.

[0048] In various embodiments, the carbon nanotubes may be contacted with or agitated with the solution of chondroitin sulfate by sonication. For example, the carbon nanotubes may be agitated with the solution of chondroitin sulfate by cup-horn sonication. In one embodiment, the carbon nanotubes may be agitated with the solution of chondroitin sulfate by cup-horn sonication in a water-ice bath. Bundles of dispersed carbon nanotubes may subsequently be removed from the suspension by centrifugation.

[0049] In yet various embodiments, the mixing may be carried out by standard mixing methods known in the art. Any suitable mixing device may be used, wherein the embodiments are not limited to a particular device. In various embodiments, the mixing may be carried out, but is not limited to, by stirring or shaking the mixture.

[0050] In various embodiments, the mixing may be carried out for about 1 to about 60 minutes, such as about 1 to about 50 minutes, about 1 to about 40 minutes, about 1 to about 30 minutes, about 1 to about 20 minutes, or about 1 to about 10 minutes. For example, the mixing time may be about 30 minutes. All mentioned time specifications may be the lower or upper limit of a respective time range.

[0051] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

Materials

[0052] Sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonic acid (SDBS), polyvinylpyrrolidone (PVP), chondroitin sulfate-A (CS-A), chondroitin sulfate-B (CS-B) and chondroitin sulfate-C (CS-C) were purchased from Sigma-Aldrich (Singapore) at the highest commercially available purity and used without further purification. Highly-purified HiPco SWNTs (super-purified grade, produced by high pressure CO conversion synthesis) were purchased from Carbon Nanotechnologies, Inc. (Houston, Texas, USA). The received SWNTs were heated in air at 350°C for 1h and refluxed in HCl (3M) for 10h. Then purified SWNTs were collected onto filter paper via vacuum filtration and washed with excess de-ionized (DI) water until the washing water dripping from the filter paper was neutral in pH. The solid on the filter paper was freeze-dried (Christ Alpha 1-2 plus Model) to a loose powder which was utilized for all subsequent purposes. CoMoCAT SWNTs (SWeNT SG65 with at least 90wt% carbon purity) were purchased from SouthWest NanoTechnologies, Inc. CoMoCAT SWNTs were used without further purification.

Preparation of CS/HiPco SWNT and PVP/HiPco SWNT solutions

[0053] To prepare CS/HiPco or PVP/HiPco SWNT solution, a mixture of HiPco SWNTs (2mg) and CS aqueous solution (CS-A, CS-B or CS-C, respectively) (10ml, 1wt%) or PVP aqueous solution was agitated by cup-horn sonication (SONICS, VCX-130) at 100W for 30min in a water-ice bath. The

suspension was then centrifuged for 1h (Sartorius, SIGMA@3K30) with 50,000g relative centrifugal force (RCF) to remove bundles of SWNTs. The homogeneous supernatant was examined spectroscopically with photoluminescence excitation (PLE) and UV-vis-NIR spectroscopy.

Preparation of SDBS/CoMoCAT SWNT solution

[0054] To prepare SDBS/CoMoCAT SWNT ultra-centrifugation solution, a mixture of CoMoCAT SWNTs (2mg) and SDBS aqueous solution (10 ml, 1wt%) was agitated by cup-horn sonication (SONICS, VCX-130) at 100W for 30min in a water-ice bath. Then the suspension was centrifuged for 1h at 60,000g RCF (Hitachi-Koki CS150GXL) to remove bundles of SWNTs. The homogeneous supernatant, denoted "SDBS/CoMoCAT", was studied and applied in field-effect transistor (FET) fabrication.

SWNT Characterization

Circular Dichroism (CD) of CS-A, CS-B and CS-C

[0055] Circular dichroism (CD) of CS-A, CS-B, and CS-C was measured on a Chirascan (Applied Photophysics Limited, UK) in a 0.1mm pathlength fused quartz cell. The scanning wavelength range was from 180 to 260nm at 0.5nm intervals. The scanning speed was 50nm min⁻¹. The concentration of polymer in D₂O was 1.0mg ml⁻¹.

Photoluminescence spectroscopy (PLE)

[0056] Measurements were conducted with a Jobin-Yvon Nanolog-3 spectrofluorometer equipped with an IGA (InGaAs) near-infrared (NIR) detector. The chiralities were determined by fitting the energy bandgaps from SWNT's E₁₁ emission when the excitation energy matches the nanotube E₂₂ energy level. For calculating the semiconducting (*n*, *m*) relative abundance distribution,

the amplitude of the partial derivative of PLE intensity versus excitation wavelength was computed following the method proposed by Arnold et al., (*Nat. Nanotechnol.* 2006, 1, 60).

Ultraviolet-visible-near-infrared (UV-vis-NIR)

[0057] Absorption spectroscopy was performed with a Varian Cary 5000 UV-vis-NIR spectrophotometer. A 10mm pathlength quartz cuvette was used for characterization.

Atomic Force Microscopy (AFM)

[0058] AFM was performed using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) in AC (tapping) mode. For AFM measurement of polymer-SWNTs solutions, the polymer-SWNTs supernatant solution was deposited onto a silicon wafer (the silicon wafer was pre-cleaned by exposure in Ar plasma (PX-500TM, March Plasma Systems, Concord, CA) for 1min with 100W discharge power at 350sccm Ar flow rate) and then rinsed for one day using neutral DI water.

Transmission Electron Microscopy (TEM)

[0059] TEM was conducted using a JEOL JEM-2010 high-resolution transmission electron microscope (HR-TEM) at 200kV. To prepare samples for the TEM, 10 μ l of supernatant solution of polymer-SWNTs after ultra-centrifugation was dropped onto a 400 mesh Lacey Formvar/Carbon-grid (PELCO, CA). Grids were dried at room temperature and then dipped into neutral DI water with shaking for 10h to rinse away the polymer.

Computer Simulations to study binding of CS-A, CS-B and CS-C with (7,6)

SWNTs

[0060] (7,6) SWNTs with length of 10nm was used in the simulation.

Aromatic carbon type without partial charge was assigned to carbon atoms of the SWNTs. Force fields of the three isomers of CS were generated with *antechamber* program; partial charge was generated with *R.E.D. III* by performing quantum chemistry (QM) calculation with widely used commercial computer software package "Gaussian with HF (Hartree-Fock)/6-31G* basis" for quantum chemistry computations, and fitted by RESP (Restrained electrostatic potential) method. The SWNT was aligned along the x-direction and a fully extended CS molecule (7-monomer length) was placed beside the SWNT. The SWNT-CS complex was placed in the centre of a 12nm×6nm×6nm box with ~13000 TIP3P water molecules. Fourteen sodium ions were added to neutralize the system because each CS monomer has 2 negative charges. All simulations were run by employing the GROMACS package (David van der et al., *J. Comp. Chem.* 2005, 26, 1701). The Amb2gmX conversion utility tool (Moblely et al., *J. Chem. Phys.* 2006, 125) was used to convert Ambe-type format to gromacs-type format. All bonds involving hydrogen atoms were constrained in length according to LINCS protocol (Berk et al., *J. Comp. Chem.* 1997, 18, 1463). The position of the SWNT was restrained at the centre of the water box by applying a harmonic force on the SWNT. This allowed the use of an integration step of 0.002ps in the simulations. Non-bonded pair lists were re-calculated every 5 integration steps or 0.01ps period. The protein and the water were separately coupled to respective external heat baths at 300K with a relaxation time of 0.1ps. Outputs of the structure snapshots or trajectories were provided every 1ps for analysis. Electrostatic interactions were treated with particle mesh Ewald method (Darden et al., *J. Chem. Phys.* 1993, 98, 10089) with a cutoff of

9Å, and a cutoff of 12Å was used in the calculations of van der Waals interactions. Two independent simulations were carried out for each CS-SWNT pair and run for 20ns. Binding free energy estimates were performed using the generalized Born (GB) implicit solvent model developed by Alexey *et al.* (*Proteins: Struct. Funct. Bioinform.* 2004, 55, 383) provided by the sander module in AMBER 9 (Case *et al.*, University of California, San Francisco, 2006).

Back-Gated SWNT FETs

[0061] Back-gated SWNT FETs were made by drop-casting CS-A/SWNT solution on p-type silicon wafers capped with thermally grown silicon dioxide layers (300nm). The source and drain electrodes were made of Au (60nm) coated on top of Ti (10nm thick). The channel width was 50μm and the length 50μm. The SWNT solution was dropped onto the devices, which were then dried and rinsed with DI water. The process was repeated until the devices formed a percolation path. The device property measurements were recorded with a Keithley semiconductor parameter analyzer Model 4200-SCS. The drain voltage was -2V and the p-type silicon was the back gate.

Results and Discussion

Comparison of Hipco SWNT Dispersion with the Three CS

[0062] The secondary structures of neat CS-A, CS-B, and CS-C polymers in solution were determined by circular dichroism (CD) spectroscopy (**Fig. 2**). The CD spectra obtained indicates that the three isomers have varying degrees of alpha-helix structure. The evidence of alpha-helicity in the structures of CS-A and CS-B are indicated by the negative peaks at 222 and 218nm, respectively, in the CD spectra. The higher absorbance at 218nm (CS-B) than at 222nm (CS-A) suggests a higher content of alpha-helicity in CS-B (27.4%) than in CS-A

(24.2%), which agrees well with the CD deconvolution data (**Fig. 3**). The spectrum for CS-C, on the other hand, suggests less α -helix structure (16.6%) in this isomer.

[0063] The three HiPco SWNTs solutions employing CS-A, CS-B and CS-C as dispersants were characterized by UV-vis-NIR and the results are shown in **Fig. 4A**. Higher absorbance generally correlates to higher solubility of SWNTs in the solution and as shown in **Fig. 4A** CS-C thus appears to have the highest absorbance while CS-B the lowest absorbance among the three isomers.

[0064] $A(S)/A(T)$ values for these three solutions were determined (Itkis *et al.*, *J. Am. Chem. Soc.* 2005, 127, 3439): $A(S)$ is the area of the E_{22} interband transition due to the nanotubes after baseline subtraction and $A(T)$ is the total area under the spectral curve due to various carbonaceous materials such as SWNTs, multiwalled nanotubes, and carbon. The $A(S)/A(T)$ ratio is an index of the ability to selectively suspend/disperse SWNTs rather than other forms of carbon in the samples. From **Fig. 4B**, it is seen that amongst the three forms of CS dispersants, CS-C selectively disperses SWNTs most effectively as it has the highest $A(S)/A(T)$ ratio of around 0.139 ± 0.011 . CS-A, with an $A(S)/A(T)$ ratio around 0.109 ± 0.004 , selectively disperses SWNTs relatively well (better than SDS) but it is not as effective as CS-C. CS-B cannot disperse SWNTs as witnessed by the low $A(S)/A(T)$ ratio of 0.045 ± 0.007 and near absence of peaks in the UV-vis-NIR spectrum of the CS-B/HiPco SWNT sample. These results show that the three isomers, though having the same chemical formulae but different spatial arrangements, have different abilities to disperse SWNTs. CS-A and CS-C have higher $A(S)/A(T)$ ratio than PVP (with an $A(S)/A(T)$ value of 0.058) as dispersant of HiPco SWNTs in aqueous solution.

[0065] Another way to quantify the nanotube concentration in the supernatant after centrifugation is with Beer's law, $A = \epsilon bc$, where A is the optical density at 500nm, ϵ is the extinction coefficient, and b is the pathlength (b is 1cm for the present cell), and c is the concentration. The respective ϵ of HiPco SWNTs solutions with CS-A, CS-B, and CS-C as dispersants was determined from the slope of the absorbance versus SWNT concentration at very dilute concentrations (fitted using linear-least-squares analysis) to be 28.6, 27.6, and 28.9 ml mg⁻¹ cm⁻¹, respectively (**Fig. 4C**). The concentrations of SWNTs in CS-A/(HiPco SWNT), CS-B/(HiPco SWNT), and CS-C/(HiPco SWNT) after 50,000g centrifugation were 0.029, 0.027, and 0.041 mg ml⁻¹, respectively, which were much higher than the respective values for SDS (0.019 mg ml⁻¹ at 120,000g necessary for debundling) (Yan *et al.*, *J. Phys. Chem. C* 2008, 112, 7579) and PVP (0.020 mg ml⁻¹) (**Fig. 5**). The yields of dispersed SWNTs in the supernatant using CS-A, CS-B, and CS-C were 14.5%, 13.5%, and 20.5%, respectively, which are comparable to or higher than those of SDS and PVP (9.9% and 10.0% respectively).

[0066] PLE spectroscopy was also used to characterize the semiconducting species of CS/HiPco SWNTs supernatant solutions (**Fig. 6A**). The species distributions with the three isomers are shown in the graphene map (**Fig. 6B**). It appears that the semiconducting nanotubes selected by the three isomers, like the SDS sample, have no particular chiral angle or diameter range (**Fig. 16**). However, the emission wavelengths of the peaks of CS-A and CS-C have undergone a red shift compared to the peaks of CS-B and SDS, as indicated by the rightward offset of the (7,6) peaks of about 10 and 11 nm, respectively, of CS-A and CS-C with respect to the vertical line passing through the same peak

of the CS-B sample (**Fig. 6A** and **Fig. 6C**). The observed red shift may be attributed to better access of water to tube surface due to a better wrapping pattern. The conformation of CS-A and CS-C might fit the surface curvatures of SWNTs better and hence disperse SWNTs better than CS-B.

[0067] To explain the different SWNT dispersion efficacies of the three CS isomers, computer simulations were carried out with heptamer CS molecules. Structure clustering with the three CS isomer molecules (without SWNTs) in water was done. The standard structures of the largest cluster obtained are shown in **Fig. 7**. The three isomers of the CS oligomers, each with 7 repeating units, adopt different conformations when they wrap around the nanotubes. CS-A and CS-C have a more extended geometry while CS-B aggregates into a ring structure. The minimum values of radii of gyration (R_g) in a 20ns trajectory for the three CS molecules (without SWNT) are 1.3nm (CS-A), 1.0nm (CS-B) and 1.4nm (CS-C). The smaller value of R_g for CS-B indicates that it is more flexible and can be easily compacted into a random coil in water. The different conformations can be explained by the different intramolecular interactions (specifically Coulombic interactions and hydrogen bonding) in the three isomeric forms of CS (**Fig. 8**). In **Figs. 8A-8C**, monomer CS repeating units are depicted for simplicity in the illustration of the significant intramolecular interactions computed. Weaker intramolecular hydrogen bonding was found to exist in CS-A and CS-C while stronger Coulombic interactions (between the $-\text{SO}_3^-$ and $-\text{OH}$) is present in CS-B. The stronger intramolecular interaction in CS-B results in a more compacted form and smaller R_g in solution.

[0068] The conformations of the three CS oligomer isomers, each with 7 repeating units, in the presence of nanotube were also computed. **Fig. 9A-C**

show that the three heptamer CS molecules tightly adsorbed around the SWNTs but adopt different conformations. CS-B wraps around the SWNT in a tighter helical manner, while the wrap patterns of CS-A and CS-C around the nanotubes are relatively more extended. For sufficiently long chains, CS-A and CS-C form helical wrappings around the SWNTs. CS-B, on the other hand, does not extend out on the nanotube surface. Considering the smallest R_g and strong intramolecular interaction for isolated CS-B, it appears that the flexible CS-B easily aggregates with itself rather than interacts with nanotubes, so that the ring pattern hinders CS-B from wrapping around carbon nanotubes (CNTs). For CS-A and CS-C, the extended geometries help them to adsorb onto and helically wrap CNTs.

[0069] During the 20ns simulations, no dissociation events between the CS molecule and SWNT occurred. The more extended conformations of CS-A and CS-C in water allow their hydrophobic main chain to approach and form stable adsorptions on SWNTs more readily than CS-B. In the models of CS-A, CS-B and CS-C wrapping around the (7,6) nanotube, it is observed that $-\text{COOH}$ and $-\text{OH}$ groups extend out into the solution and that $-\text{NHCOCH}_3$ group align almost parallel to the nanotube axis, while H atoms of the backbone are inside the helical structures and interact with the nanotube sidewalls (**Fig. 9D**). For all the CS isomers, the hydrophobic surface is in contact with the nanotube, leaving hydrophilic groups (such as $-\text{SO}_3$, and $-\text{COO}$) outside of the coil. The height of polymer on the CNT is estimated to be around 0.8nm for CS-A and CS-C through the radial distribution function of CS-A (or CS-C) with respect to the surface of CNT.

[0070] Estimations of the respective SWNT-CS binding energies were done to investigate the differential interactions of the CS isomers with the SWNTs.

The binding energy of a SWNT-CS complex was calculated as follows:

$$E_B = E_C^{GB} - (E_P^{GB} + E_T^{GB})$$

where E_C^{GB} , E_P^{GB} , and E_T^{GB} are the energies of SWNT-CS complex, CS polymer and nanotube, respectively, based on the implicit GB model. The binding energies of the five main SWNT species in HiPco samples (i.e. (7,5), (8,4), (10,2), (7,6), and (9,4) with diameters from 0.829 to 0.966nm) were calculated. The binding energies listed in **Fig. 10A** and **Fig. 11** indicate that the binding of CS-B with each chiral SWNT is much weaker than CS-A or CS-C. There is not much difference between the binding energies of CS-A and CS-C with SWNTs. Considering the simplicity of the computational model employed here, e.g. no partial charges on the SWNTs, the resolved differential binding of different CS isomers on the SWNTs may be primarily due to their different conformations around the SWNTs. The binding energy between polymer and SWNT appears to be related to the SWNT's diameter for the better dispersing CS-A and CS-C (**Fig. 11**). Species (7,5) and (8,6) have similar chiral angle, but the binding energy of polymer/(8,6) SWNT with larger nanotube diameter (0.966nm) is higher than that of polymer/(7,5) SWNT with smaller nanotube diameter (0.829nm). Our data also suggest no correlation of binding energy with chiral angle within the values studied (**Fig. 12**).

[0071] The removability of CS-A and CS-C from HiPco nanotubes with washing was examined by XPS and compared with SDS. SDS/HiPco and CS/HiPco solutions were filtered onto filter paper and washed with excess water. The nanotubes on the filter papers were then characterized with XPS

(**Fig. 10B**). SDS data showed that some residual sulfur (S) remains although this surfactant can be removed by washing with water. In the CS-A/HiPco and CS-C/HiPco samples, there are also very low S contents, illustrating that most of the CS isomers have been washed away. Typically, polymeric dispersants cannot be removed easily but CS appears to be more readily removable than other polymers that interact with nanotubes via π - π stacking. By comparison with polymers having π - π interactions with nanotubes, the interaction of CS-A and of CS-C with nanotubes is likely not to be so strong as to prevent its removal. Also, CS wraps around nanotube without alteration of the nanotube's intrinsic structure (**Fig. 13**, Raman results). The removal of dispersant/surfactant from nanotubes after dispersion is critical for applications in electronic devices, for example.

[0072] The TEM image (**Fig. 14A1**) shows that using CS-A, the nanotubes are well-dispersed into individual tubes. The AFM image (**Fig. 14A2**) corroborates the observation that CS-A can disperse SWNTs into individual nanotubes with less than 1nm diameter. Most of the polymer chains have been washed away since water had been passed over the samples for 10min. For CS-B/(HiPco SWNT) solution, the TEM image (**Fig. 14B1**) shows bundles of SWNTs. The height profiles of the corresponding AFM pictures (**Fig. 14B2,B3**) indicate that the SWNTs exist as bundles with diameter of ~10nm, which indicates poor dispersion by CS-B. For CS-C/(HiPco SWNT), the TEM image (**Fig. 14C1**) shows individually dispersed SWNTs, though there is polymer wrapped around them. The height profile of the corresponding AFM picture (**Fig. 14C2**) shows that the nanotubes exist as individual tubes (with height of around 1nm), co-mingled with small bundles (few nm in diameter) together with some

polymer (seen as white speckles) left even under the same washing condition as for CS-A/HiPco samples.

[0073] Further, higher magnification AFM images (**Fig. 14A3,C3**) show periodic wavelike height profiles for two of the CS, viz. CS-A and CS-C. The AFM image of **Fig. 14A3** shows helical wrapping of CS-A of ~ 0.7 nm thick around the SWNTs, which corroborates the CS-A wrapping seen in the TEM image (**Fig. 14A1**). Periodic wavelike profiles with height of ~ 0.7 nm in the AFM image (**Fig. 14C3**) also indicate helical wrapping of CS-C around the SWNT. The poor solubility of CS-C results in the polymer not being easily washed away as shown by the thick residual polymer left on the nanotubes seen in the TEM and AFM pictures (**Fig. 14C1,C3**). From the periodic wavelike height profiles of CS-A and CS-C (**Fig. 14A3,C3**), the height of the polymers on the nanotubes is found to be about ~ 0.5 – 1.0 nm, which is corroborated by the calculated thickness of 0.8 nm by the simulation described above.

[0074] To prove the easy removability of CS-A, network field-effect transistor (FET) devices using CS-A/CoMoCAT® SWNT solution were fabricated. As-synthesized HiPco SWNTs cannot be used to fabricate devices that are switchable as they have a wide chirality distribution with too many metallic nanotubes. CoMoCAT® SWNTs have few chiralities, higher semiconducting nanotube content as supplied, and shorter tube length, so that some devices can be switched on and off even without metallicity-based separation. If a thick layer of residual polymer remains, the current through the SWNT network will be negligible. **Fig. 15A** shows the typical charge transfer properties of CS-A/CoMoCAT® solutions with forward and reverse sweeps of drain current (I_d) versus gate voltage (V_g) at constant drain voltage. **Fig. 15C** shows a histogram

of the percentage of devices with different on/off ratios. Devices using CS-A/CoMoCAT® have on/off ratios of 10^1 – 10^3 , similar to those made using SDBS/CoMoCAT®. AFM of the nanotubes in the channel between the electrodes (**Fig. 15B**) shows that CS-A has been mostly removed. The good solubility of CS-A in water (100 mg ml^{-1}), particularly in the presence of sodium counter-ions, is believed to cause its easy re-dissolution.

[0075] It has been found that CS-A and CS-C, in contrast to CS-B, polymers are good SWNT dispersants. The different spatial arrangements of the functional groups in the different isomers lead to different intramolecular interactions and polymer conformations, and hence differing nanotube dispersion efficacies. Weak intramolecular interaction, extended polymer conformation and a balance of hydrophobic and hydrophilic segments of an isomeric form of a polymer all contribute to good nanotube dispersibility. The present water-based CS dispersant disperses SWNTs as well as small molecular surfactants such as SDS and may find applications in biocompatible hydrogels or in some nanotube inks which need to have reasonably high surface tension, such as in inkjet printing, for example. The removal of dispersant/surfactant from nanotubes after dispersion is particularly important for electronic applications. Due to the presence of significant metallic species, better transistor-based device performance may be obtainable and improved by patterning the nanotube network to suitable width to decrease the percolation of metallic nanotubes.

[0076] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that

the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0077] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0078] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0079] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

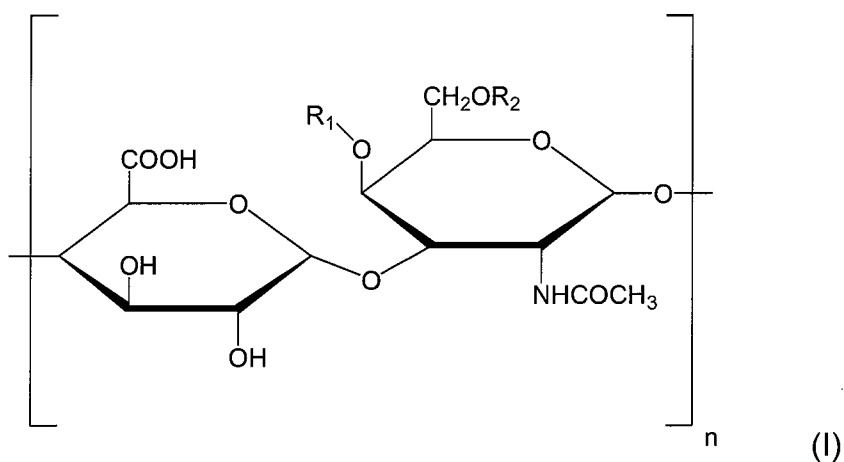
[0080] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the

generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0081] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

1. A method for dispersing carbon nanotubes, comprising:
- (a) providing a solution containing chondroitin sulfate cation salt of formula (I)



wherein

R_1 is H and R_2 is MSO_3 ;

M is an alkaline metal, or an alkaline earth metal further bound to a monovalent counter-anion;

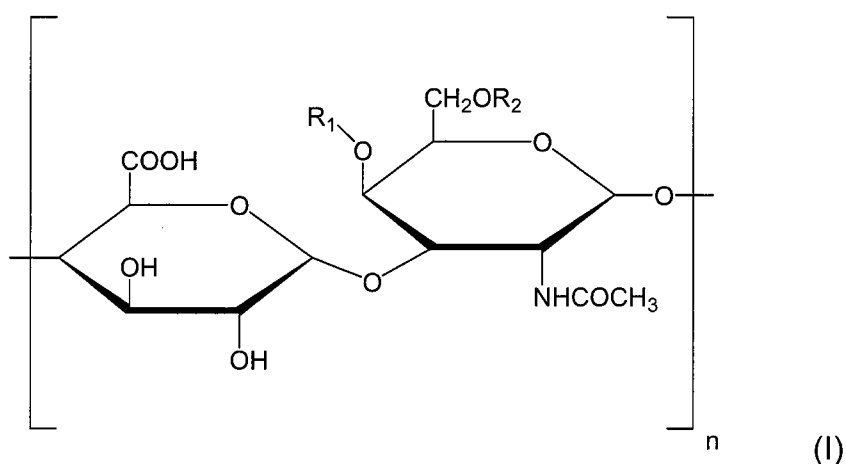
n is at least 20; and

- (b) contacting the carbon nanotubes with the solution containing the chondroitin sulfate cation salt.

2. The method of claim 1, wherein M is selected from the group consisting of sodium, potassium and calcium.

3. The method of claim 2, wherein M is sodium.

4. The method of claim 2, wherein M is calcium and the monovalent counter-anion is selected from the group consisting of chloride, bromide, iodide, chlorate, nitrate and nitrite.
5. The method of any one of claims 1-4, wherein the carbon nanotubes are single-walled carbon nanotubes.
6. The method of any one of claims 1-5, wherein contacting comprises agitating the mixture of carbon nanotubes and the solution by sonication.
7. The method of any one of claims 1-6, further comprising centrifuging the mixture of carbon nanotubes and the solution to separate the dispersed carbon nanotubes from the mixture.
8. Use of a chondroitin sulfate cation salt for dispersing carbon nanotubes, wherein the chondroitin sulfate cation salt has formula (I)



wherein

R_1 is H and R_2 is MSO_3 ;

M is an alkaline metal, or an alkaline earth metal further bound to a monovalent counter-anion;

n is at least 20.

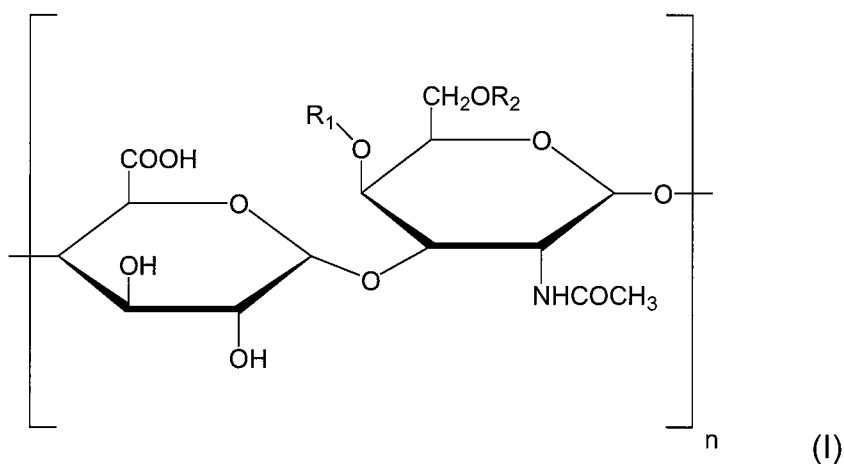
9. The use of claim 8, wherein M is selected from the group consisting of sodium, potassium and calcium.

10. The use of claim 9, wherein M is sodium.

11. The use of claim 9, wherein M is calcium and the monovalent counter-anion is selected from the group consisting of chloride, bromide, iodide, chlorate, nitrate and nitrite.

12. The use of any one of claims 8-11, wherein the carbon nanotubes are single-walled carbon nanotubes.

13. A carbon nanotube having a chondroitin sulfate cation salt attached thereto, wherein the chondroitin sulfate cation salt has formula (I)



wherein

R_1 is H and R_2 is MSO_3 ;

M is an alkaline metal, or an alkaline earth metal further bound to a monovalent counter-anion;

n is at least 20.

14. The carbon nanotube of claim 13, wherein M is selected from the group consisting of sodium, potassium and calcium.
15. The carbon nanotube of claim 14, wherein M is sodium.
16. The carbon nanotube of claim 14, wherein M is calcium and the monovalent counter-anion is selected from the group consisting of chloride, bromide, iodide, chlorate, nitrate and nitrite.
17. The carbon nanotube of any one of claims 13-16, wherein the carbon nanotubes are single-walled carbon nanotubes.
18. A field-effect transistor comprising a carbon nanotube of any one of claims 13-17.
19. Use of a carbon nanotube of any one of claims 13-17 in conductive and high-strength nanotube/polymer composites, catalysts, transparent electrodes, sensors and nanoelectromechanical devices, additives for batteries, radiation sources, semiconductor devices, ultracapacitors or interconnects.