



A Critical Review of the Role of Carbon Nanotubes in the Progress of Next-Generation Electronic Applications

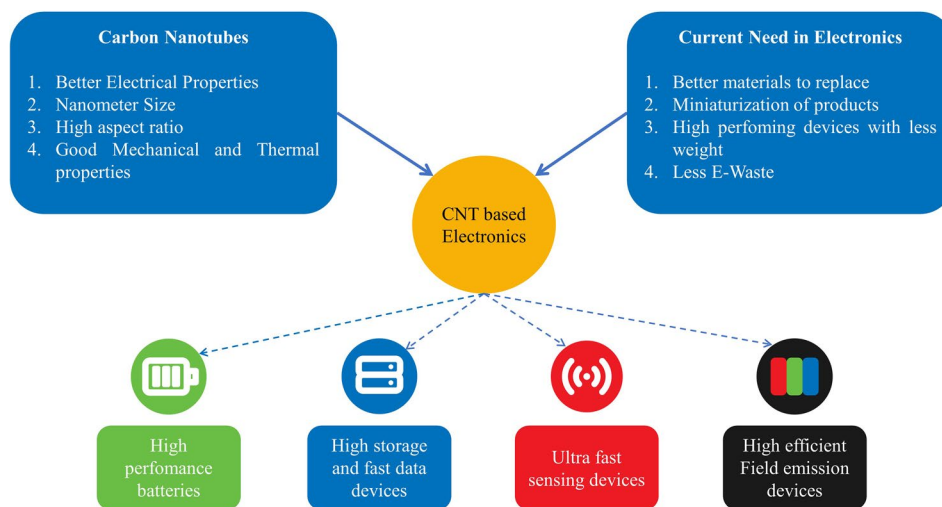
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Abstract

Electronic products are becoming an essential part of our daily life. There is a huge demand to produce small and portable but powerful electronic products. Carbon nanotubes (CNTs) have excellent electrical, mechanical and thermal properties which can be exploited to build next-generation electronics. This paper reviews different types and properties of CNTs and also presents the CNT-based electronics along with their advantage over the conventionally used products. CNT usage in electronics, such as biosensing, energy and data storage devices, is discussed. CNT-based field emission devices, which showed outstanding results are also discussed. The current challenges of CNT-based electronics and the future of CNT in electronics applications are mentioned.

Graphical Abstract



Keywords Carbon nanotubes · properties of CNTs · electronics applications

Introduction

Cylindrical fullerenes, called carbon nanotubes (CNT), were discovered by Sumio Iijima in 1991. He found carbon nanotubes in the soot of evaporated carbon from the arc discharge of graphitic electrodes.^{1,2} CNTs have a seamless cylinder-like structure constructed from rolling up of graphite sheets with nano-range diameters.³ The

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hexagonal atomic lattice, sp^2 hybridization and interplanar distance of 0.335 nm remain the same in CNTs as in graphite.³ CNTs have many useful characteristics which include high yield strength, higher length-to-diameter ratio exceeding 1000:1,⁴ higher surface area,⁵ ballistic electron conduction,⁶ high capacitance,⁷ better electrostatic properties,⁸ more stability at higher current⁹ and higher Young's modulus.⁸ The concentration of CNT in a nanocomposite increases the specific volume fraction to transition from insulator to conductor which is called the percolation threshold.¹⁰ The amount of CNT added to a polymer nanocomposite was found to have low volume fraction of about 0.01% to achieve high electrical conductivity.⁶ The polymer-CNT network acts as a better gas transport system by providing 100 times greater gas flow than the theoretical model (Knudsen model of gas transport).¹¹ Less molecular collision and friction with the CNT walls are found to increase the gas flow in CNTs.¹¹ CNTs are produced primarily by three methods: Arc discharge, laser ablation and chemical vapor deposition (CVD). Arc discharge CNTs are produced by creating a high potential arc between a graphitic cathode and an anode which results in the formation of CNTs with many impurities at the cathode,^{4,12} whereas laser ablation uses *Nd:YAG* (neodymium-doped yttrium aluminium garnet) laser to evaporate the target material to produce CNTs.¹² Chemical vapor deposition is the most preferred economical way to produce CNTs. The process involves the pyrolyzation of a hydrocarbon source in an inert atmosphere producing free carbon vapor. The vaporized carbon is deposited in a transition metal catalyst to form carbon nanotubes.¹² CNTs open up possibilities for endless applications such as drug delivery in medicine,¹³ frictionless transport chains,¹¹ filters in water purification,¹¹ conductive composites,⁶ data storage devices,¹⁴ batteries and transistors in electronics.⁸ Electronics remain a lucrative industry for the application of CNTs. CNT-based electronics can produce small,

lightweight, and low power-consuming products. Field emission of CNT is used in scanning electron microscopy (SEM) as an electron source and is found to give higher order of brightness than the conventional metal tips.⁶ CNT-based transistors are reported to have less leakage current.¹⁵ CNT-based cathode ray tubes (CRT) give higher efficiency and more luminescence than conventional ray tubes.¹⁶ CNT electrodes in lithium-ion batteries store more lithium than graphite, giving increased energy density.^{17,18} This paper has put together some fascinating applications of CNT in the electronics industry.

Types of CNTs

CNTs are classified into two types: (1) single-walled carbon nanotubes (SWCNTs) and (2) multi-walled carbon nanotubes (MWCNTs). SWCNTs were found by Sumio Iijima and Toshinari Ichihashi in 1993.¹⁹ The single-walled carbon nanotube has a structure of a seamless cylindrical tube made up of one layer of graphene by rolling it from edge to edge. SWCNTs have a diameter of 1 nm, and the length can range up to 1 mm. SWCNTs are more expensive to produce than MWCNTs.⁴

A MWCNT has concentric tubes of graphene sheets with varying diameters. The interplanar distance between each of the concentric cylinders is found to be in the range of 0.32 nm to 0.35 nm.²⁰ This distance is nearly the same as the interplanar distance between the graphene layers in graphite.⁴ Most electronic applications use MWCNTs rather than SWCNTs. This is due to the improper adhesion of SWCNTs on the appliance substrate,¹⁴ whereas MWCNTs have more active sites at the end of the tube¹⁸ (due to the presence of more concentric tubes) giving better adhesion with the substrate.¹⁴ There is a special type of MWCNT called the double-walled carbon nanotube (DWCNT). DWCNTs contain only two concentric

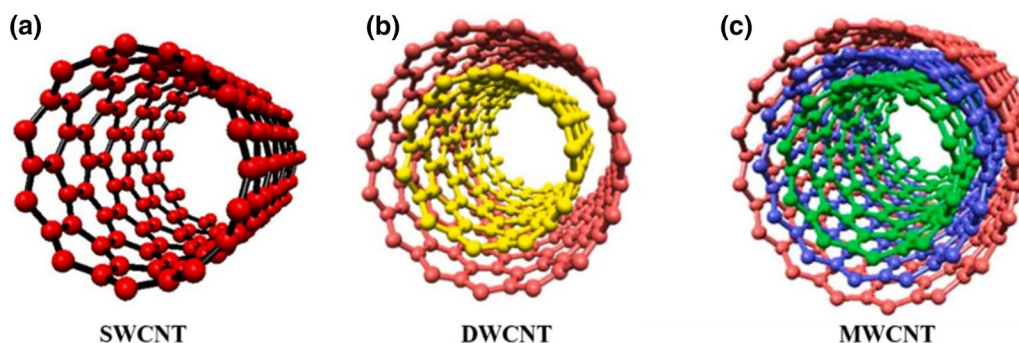


Fig. 1 Schematic structure of defect-free (a) SWCNT, (b) DWCNT, (c) MWCNT (reprinted from reference 21, under the terms of the Creative Commons CC BY license).

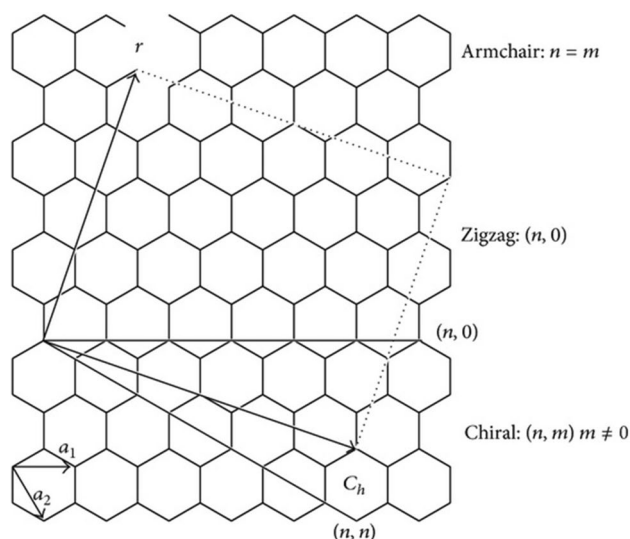


Fig. 2 A schematic image of components of the chiral vector \vec{C} and the direction of nanotube axis for armchair, zigzag and chiral CNTs (reprinted from reference 4, under the terms of the Creative Commons CC BY license).

cylinders of graphene layers with an interlayer space of 0.335 nm. The DWCNT has very similar properties to the SWCNT.⁴ Figure 1 shows the structure of SWCNTs, DWCNTs and MWCNTs.

Based on chirality, CNTs are classified into armchair, zigzag and chiral nanotubes. The chirality of a CNT is determined by the chiral vector, $\vec{C} = n\vec{a}_1 + m\vec{a}_2$ where n and m are integer values, and \vec{a}_1 and \vec{a}_2 are the unit cell vectors of the rolled graphene sheet (Fig. 2).

The types of CNTs based on the chirality property vary in the ratio of $n:m$ for armchair, zigzag and chiral nanotubes. For armchair CNTs $n=m$, for zigzag CNTs, $n=0$ and for chiral nanotubes, $n:m$.¹² The chiral vector (n, m) determines the chiral angle ($\cos\theta$) and the diameter (D_{CNT}) of CNTs.²²

$$\cos\theta = \frac{n + m}{2\sqrt{n^2 + m^2 + nm}} \quad (1)$$

$$D_{\text{CNT}} = \sqrt{3}a_0 \frac{\sqrt{n^2 + m^2 + nm}}{\pi} \quad (2)$$

The ratio $n:m$ is a parameter which determines important properties of CNT such as the volume fraction in nanocomposites. CNTs with 1–2-nm diameter (which is purely dependent on chirality) are found to have lower volume fraction in nanocomposites than that of CNTs with larger diameter.¹⁰ A schematic image of armchair, zigzag, and chiral nanotubes are shown in Fig. 3.

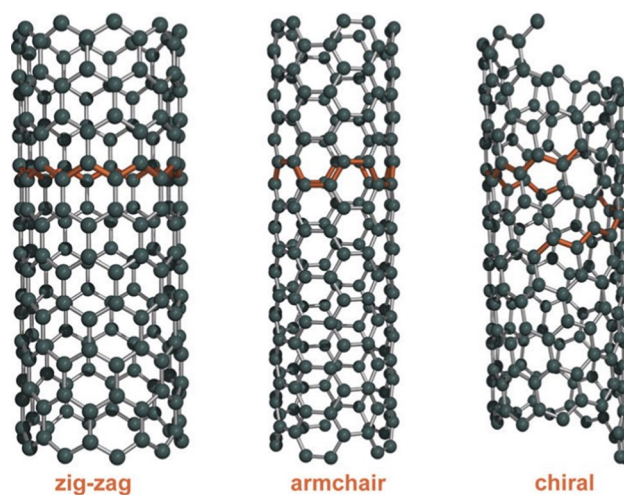


Fig. 3 Schematics of zigzag, armchair, chiral SWCNT (reprinted from reference 1, under the terms of the Creative Commons CC BY license).

Properties of CNTs

Electrical Properties of CNTs

CNTs are used mainly in electronics due to their remarkable current density of 10^9 A/cm²⁶ and specific capacitance. The specific capacity of a CNT sheet-type electrode of 25.4- μm thickness is found to be in the range of 39.2–90.4 F/cm³.⁷ CNTs can be semiconductors or conductors depending upon the type of architecture.¹² The electric conductivity, resistivity²³ and capacitance⁷ of CNTs can be altered to a certain extent by functionalizing them with the appropriate chemical functional groups. CNTs doped with gold nanoparticles create covalent bonds on the surface of the fibers, showing an increase in conductivity.²³ Chemical treatment can increase the electrochemical performance of CNTs by opening the cap.¹⁷ Heat treating CNTs in a gas atmosphere lowers their conductivity by forming sp^3 bonds with the gas.²³ SWCNTs show a 23% increase in energy density over graphite.¹⁸ The electrical properties change as the chirality, temperature, defects and atmosphere change.²³ Comparatively, MWCNTs have a higher electrical conduction than SWCNTs.²³ Pure SWCNTs show electrical resistivity of 10^{-6} Ω cm, whereas commercially produced SWCNTs (by CVD) show an electrical resistivity of 1×10^{-4} Ω cm to 7×10^{-4} Ω cm. The variation in resistivity may be caused by the impurities and defects produced in the manufacturing process. It is also reported that CNTs show variation in their electrical properties due to their interfacial contact resistance.²³ The contact resistance is created when two CNTs are connected. It is shown that when the contact area between the CNTs increases, the contact resistance decreases. Longer CNTs with an increased contact area on their interfaces

show 49.5% increase in the conductance compared to the CNTs without interfacial contact.²³ CNTs are known to form a Schottky barrier connection with the matrix, which enhances the recovery time and reduces the turn-on voltage. This makes CNTs a promising candidate for use in field emission transistors.²⁴ Table I gives the electrical conductivity of CNTs from different experiments. A simulation study revealed that a CNT can hold voltage up to 20 V/nm, after which it starts to unravel to a trumpet shape.⁸ The critical voltage for unravelling to occur can vary according to the atomic arrangement (chirality). CNTs of chirality (6, 0) and (5, 5) were found to reach their critical voltage when the total charge of the tube reached $+39e$ and $+34e$ (where e is electric charge), respectively.⁸ Closed CNTs have higher critical voltage than open CNTs due to the presence of the pentagonal cap at the end, making them stable for more time than the open ended ones.⁸

Mechanical Properties of CNTs

The mechanical properties of CNTs can show variation for many reasons, such as the method of production, number of defects, and structure, diameter, and symmetry of nanotubes.^{1,29} A study in which arc-grown and catalyst-grown MWCNTs were tested for strength resulted in arc-grown MWCNTs with higher strength than the other. This is because there are fewer defects in arc-grown MWCNTs than catalytic-grown MWCNTs.²⁹ Practically, ideal CNTs cannot be produced on a large scale, and thus there are no standard chart values for the moduli of CNTs. The covalent sp^2 bonding in CNT plays a major role in their strength.²⁹ It

is shown that MWCNTs can be bent at higher angles without destroying the structure.³⁰ The bending strength of MWCNTs with large diameters was found to be 14.2 ± 0.8 GPa.²⁹ In early times, it was very difficult to measure the strength/Young's modulus of CNTs due to their small dimension.²⁹ Later, transmission electron microscopy (TEM) was used to observe the Young's modulus of SWCNTs and MWCNTs. For MWCNTs, the highest Young's modulus recorded was 4.15 TPa, and for SWCNTs, it was around 1.3 TPa.^{29,30} This method was found to have many errors in measurement.³⁰ Atomic force microscopy (AFM) was then used to apply pressure on CNTs and the load-displacement curves were plotted to directly obtain the Young's modulus. A Si_3N_4 AFM tip was used for applying force on the MWCNTs and SWCNTs. MWCNTs (26–76-nm diameter) recorded a Young's modulus of 1.28 ± 0.59 TPa and SWCNTs were around 1 TPa.²⁹ Many theoretical simulations and experimental results were found and the values were similar in some cases only.^{29,30} Many researchers used SWCNTs for their study because SWCNTs have fewer defects than MWCNTs and so exhibit more strength.³⁰ Table II shows the different values of Young's modulus obtained by either the modification or experimentation of CNTs.

Thermal Properties of CNTs

The thermal properties of CNTs mainly depend on the acoustic phonons of the nanotubes.³ The mean free path of phonons determine the range of thermal conductivity of the CNT.³ The specific heat of SWCNTs at varying temperatures

Table I The different values of electrical conductivity recorded by different authors during the experimentation of CNTs

Method of experimentation/modification of CNT	Electrical conductivity of cnt (Megasiemens per meter (MS/m))	References
Cu-CNT nanocomposite produced by flake powder metallurgy	47.85 ± 0.64	25
CNT filled epoxy nanocomposite mixed at 500 rpm for 60 min	3.34×10^{-9}	26
$MgFe_2O_4$ nanopowder catalyzed CNT sponge	2.08×10^{-4}	27
Polylactic acid-CNT(8 wt.%) based printed parts using fused deposition modeling	1.00×10^{-8}	28

Table II The reported values of Young's modulus for varying experimentation or modification on CNTs

Method of modification/experimentation of CNT	Type of CNT	Young's modulus (TPa)	References
Bar model of CNT	SWCNT	2.8–3.6	31
	MWCNT	1.7–2.4	
Direct tensile load testing	SWCNT	0.32–1.470	32, 33
	MWCNT	0.27–0.95	
Cantilever model of MWCNT tested by atomic force microscopy	MWCNT	1.28 ± 0.59	34
Simply supported beam model for MWCNTs grown via arc method	MWCNT	1 (approx.)	35

is compared with 2D graphene, 3D graphite and 3D SWCNT rope in Fig. 4. As CNTs have a 1D cylindrical tube structure formed by folding a 2D graphene sheet, the phonon band structure becomes stiffer in the CNT.³⁶ The phonon density of states (PDOS) of isolated SWCNTs remains constant at low temperature resulting in populated acoustic phonon modes. This eventually leads to the linear dependence of specific heat above 1 K.³ As the temperature reaches 6 K, the slope of specific heat increases, as represented in Fig. 4 because of the increased population of optical subbands.³⁶ The temperature dependence below 1 K is comparatively different from the dependence above 1 K. Below 1 K, the increased population of transverse phonons causes a specific heat temperature dependence of $T^{0.62}$. As the temperature exceeds 1 K, the population of longitudinal and acoustic phonons increases resulting in a linear specific heat curve, as shown in Fig. 4. The specific heat of the SWCNT rope, 3D SWCNT and graphene were found to coincide and reflect the phonon structure of 3D graphite at high temperature.³⁶

Certain experiments evaluated the thermal conductivity of CNTs at room temperature and the value was around 6600 W/m K.³⁶ SWCNTs and MWCNTs were measured to have

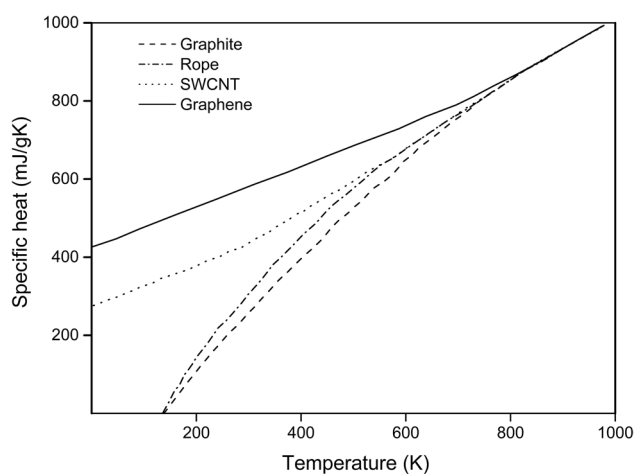


Fig. 4 The graph of specific heat vs. temperature of graphene, graphite, SWCNT rope and SWCNT (data from reference 36).

thermal conductivities of 200 W/m K³⁶ and 3000 W/m K³, respectively. The thermal properties obtained by different techniques of measurements of SWCNTs and MWCNTs are given in Table III.

Electronic Applications

As this paper focuses on CNT-based electronics, the uses of CNTs in field emission, data storage, energy storage, bio-sensing, nanoelectromechanical systems and super capacitors are explained in the following sections.

Field Emission Technology

Field emission basically means the emission of an array of electrons at specified locations. Field emission has many uses, such as an electron source for SEM, TEM and AFM^{6,9} in transistors¹⁵ and in flat panel displays.⁹ A good field emitter should have a very small tip structure,¹² a low gate voltage, reduced sensitivity to current¹² and a high current density. Conventional elements used for field emission include anisotropically etched silicon and tungsten.⁶ CNTs have a current density of 10⁹ A/cm²⁶ before the initiation of electromigration. The threshold voltage for field emission is found to be low at 1–3 V/m for SWCNT film,⁹ whereas Si tips have a threshold voltage starting at 50 V/m. From Eqs. 1 and 2, the threshold voltage can be obtained as

$$V_{th} = \frac{aV_{\pi}}{\sqrt{3}qD_{CNT}} \quad (3)$$

From Eq. 3, the magnitude of the threshold voltage can be controlled by the diameter while the direction of voltage depends on the chiral angle.²²

CNTs use only 6% of the current used by conventional emission tips. It is also reported that a CNT has better field emission than any other carbon allotropes.¹² MWCNTs grown in hydrogen have a narrow central cavity and the innermost diameter is found to be around 0.1 nm which is smaller than the pristine MWCNTs grown in helium and

Table III The thermal conductivity of types of CNTs obtained from different measurement techniques

Method of measurement/technique used in CNT	Type of CNT	Thermal conductivity (W/m K)	References
Four-point probe 3- ω method	Single MWCNT MWCNT covered with Pt	650–830	37
Four-point probe 3- ω method	Single MWCNT	300 \pm 20	38
Phase-sensitive transient thermoreflectance (PSTTR)	MWCNT	244	39, 40
Photothermal technique	Vertically aligned MWCNT film (along the axial direction)	0.145	41
Nanosecond thermoreflectance	Metal coated vertically aligned SWCNT	> 8	42

even SWCNTs. These CNTs are considered rods or fibers for their mere absence of a central cavity and are called graphitic nanofibers or nanografibers.¹⁶ These nanografibers are found to have a higher current than MWCNTs (pristine MWCNTs grown in helium).¹⁶ CNTs can be a better replacement for the conventional elements as they have many suitable properties for higher field emission.

Field Emission Transistors

Field emission transistors (FET) are used in amplifiers, oscillators, current choppers, limiters etc. A metal oxide semiconductor field effect transistor (MOSFET) is commercially used in many fields for frequency applications and is mostly made of silicon.²² The ability to change electrical conduction based on the applied voltage is the principle of a MOSFET. The silicon-based electronic devices tend to fail eventually when the channel width is reduced below 10 nm, and thus there is a need for alternatives to achieve ultra-small electronic integration for future devices.²² A CNT-FET has the same working principle as a MOSFET.²² CNT-based FETs were reported to show less quantum capacitance at higher voltage while MOSFETs start to degrade. It is also shown that temperature has a negligible effect on the function of a CNT-FET while a MOSFET tends to fail.²² Figure 5 depicts a schematic diagram of a CNT-FET. A method of production of a CNT-FET by Kilnke¹⁵ involves functionalizing CNTs with hydroxamic acid as the first step. Then the functionalised CNTs are deposited into a pre-oxidized aluminium strip boundary on a silicon substrate, and as a final step, annealing to $\sim 600^\circ\text{C}$ is done to remove the functionalization entirely to restore the properties of the CNT.¹⁵ Palladium leads are connected as source and drain.¹⁵ This CNT-based field emission transistor (CNT-FET) showed a very small gate voltage of ± 0.5 V. The on-to-off current ratio is found to be more than 10^6 .¹⁵ A CNT-FET can be used in high-frequency applications, as it has an 8-GHz current cutoff frequency.¹²

Y-junctions are also found to have application in FETs. The addition of titanium (Ti) vapor in the form of

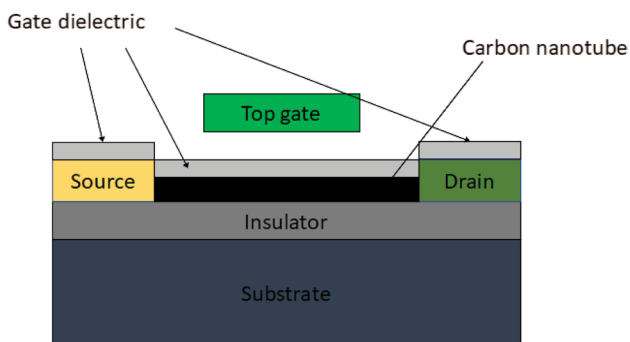


Fig. 5 A schematic image of CNT-FET (adapted from 22).

a precursor in chemical vapour deposition (CVD) can initiate the growth of Y-junction nanotubes. It is found that using a metallocene (ferrocene + xylene) mixture together with $\text{C}_{16}\text{H}_{40}\text{N}_4\text{Ti}$ within the concentration of 0.75% as the precursor induces the growth of CNT in CVD. It occurs in three stages. In the first stage, a small amount of Ti precursor together with a high-carbon source vapor is released. This starts the growth of the nanotube (at $\sim 150^\circ\text{C}$). Then, the Ti precursor concentration is increased and the carbon source is reduced to a minimum for some time. In this step, metal-rich Ti containing catalyst particles settles on the walls of the MWCNT to initiate the Y junction growth (at 750°C) as in Fig. 6. Then, the Ti precursor can be reduced gradually and the carbon source can be increased for the growth of carbon nanotubes from the Y-junctions. By using Ti vapor as a precursor, spontaneous growth of CNTs is observed. After the process, 90% of the MWCNTs formed contain Y junction(s).³⁷ A continuous supply of the Ti precursor gives rise to the cascading of Y-junctions in the nanotubes. Cascading Y-junction nanotubes can be used as electrical signal splitters for frequency media. A four-branch Y-junction CNT can be used as a double-gated FET.³⁷

Field Emission Displays

The market demands more advancement in the conventional silicon-based field emission displays (FED) that are more bendable with low power. A CNT-FED is a potential alternative as it consumes much less power, has high brightness and also is stable at high current.⁹ They are reported to have higher response at a wider temperature range with low power usage.^{6,9} To have better control over the grey scale, a triode structure is always preferred.³⁸ Field emission display elements are of two kinds commercially, vacuum fluorescence display (VFD) and cathode ray tube (CRT).¹⁶

The CNT-CRT is reported to have two times deeper luminescence with a lifetime of 8000 h in vacuum, whereas conventional CRTs require ultrahigh vacuum.¹⁶ CNT-CRTs have luminescence of $2.3 \times 10^4 \text{cd/m}^2$ for red, $6.3 \times 10^4 \text{cd/m}^2$ for green, and $1.5 \times 10^4 \text{cd/m}^2$ for blue at $200\text{-}\mu\text{m}$ anode current.¹⁶ The CNT-VFD is also found to have the same luminescence as the CNT-CRT. But they showed an increase in applied voltage for the anode.

In 4.5 and 9 inches of CNT-FEDs, CNTs were grown vertically on metal plates on cathode. The CNT-FED setup is done in an argon and hydrogen atmosphere at around 415°C . The anode consisted of ITO (indium tin oxide) coating and primary colour pixels. They resulted in less emission due to the effect of crosstalk between the pixels. So, an edge field effect CNT-FED was built by coating CNTs only on the edge of the metal substrate. This prevented the crosstalk between pixels and stable images were formed.³⁸

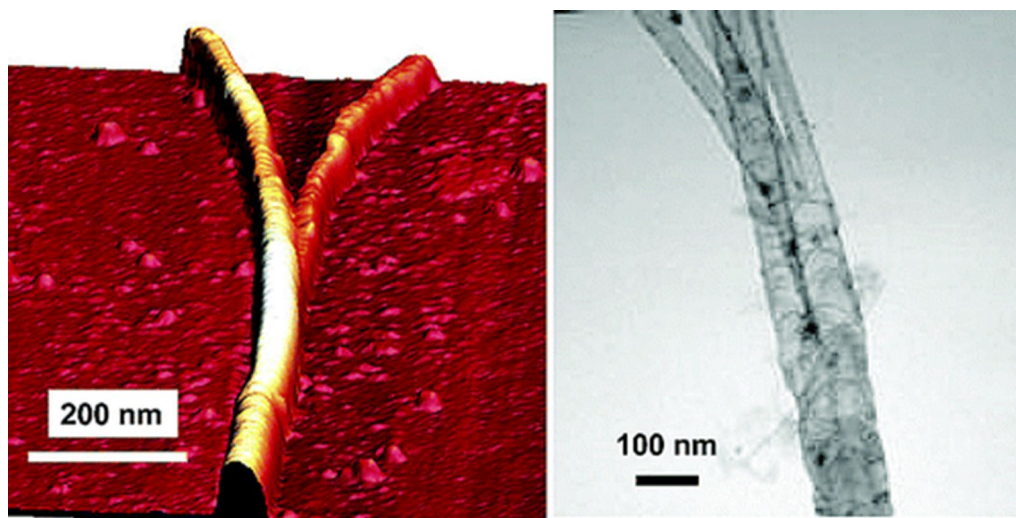


Fig. 6 A microscopic image of a Y-junction in a CNT (reprinted with permission from 37, Gothard et al., Nano Letters 2004, 4, 2, 213–217. © 2003, American Chemical Society).

An approach by Riyajuddin,³⁹ in which seamless pure graphene and a vertically grown CNT heterostructure (SGVCNT) was developed using thermal CVD and plasma-enhanced CVD. As the structure aligned vertical CNTs, the length and diameter were recorded to be about 55–60 μm and 5–6 μm . The heterostructure was placed on a non-active Si/SiO₂ substrate and checked for field emission properties. The seamless interface of SGVCNTs resulted in less interface barrier resistance, thus increasing the current density up to 236 mA/cm². This current density is higher than the graphene-based FED studies by Lee⁴⁰ and Ratha.⁴¹

Biosensing Applications

Commercially produced CNTs have many impurities such as Al₂O₃ and transition metal catalysts such as Fe, Co, and Ni, so there are many steps of purification before using CNTs in biosensing. After purification, functionalizing the CNT according to the biosensing atmosphere takes place. Surface modification and functionalization of CNTs actually decreases the electrical conductivity of the CNT by changing the *sp*² bonding to *sp*³.¹³ CNTs are coated with semi-permeable nafion to reduce the reaction with chemicals such as uric acid and ascorbic acid.¹³ Functionalization of CNTs with amino acid increases the covalent nature of a CNT towards the biological atmosphere, thus resulting in more physical absorption.¹³ Human cells and tissue are found to be transparent to the fluorescence of a CNT, as it falls near the infrared region.³⁰ CNTs only need very low potentials for detection, but have faster and higher detection compared to conventional electrodes.¹³ Basic assay tests are more expensive and take more time while CNT-based tests are inexpensive, quick and simple.¹³

There are many uses for a CNT in biosensing, and some are listed in Table IV.

Data Storage Devices

The portability of electronics can be determined by building and integrating small and powerful data-storing devices. New technologies such as magneto-resistive random access memory (MRAM), phase-change memory RAM (PRAM) and many others are leading the way to non-volatile and quicker data storage than the conventional ones.¹⁴ Nantero Inc. has recently developed a nano-RAM (NRAM) technology which is in the development phase and soon will be available on the market. Data devices developed from CNTs are reported to have a profitable future on the market.¹⁴ CNT-based data-storing devices can be built in cantilevered, suspended, vertical and telescoping CNTs.

Cantilevered CNT-Based Data Storage

A CNT is connected to the source of a three-terminal cell, while the gate and drain are below on the Si substrate. As CNTs with smaller diameters are reported to have adhesion problems with the metal electrode, CNTs with a larger diameter are chosen for this device.

When voltage is applied between the gate and the source, the CNT electrode bends and makes electrical contact with the drain (Fig. 7b). Now, the state of the device is conducting 1'. CNTs tend to reflect much time from the drain before making the electrical contact. This causes phonon excitation in the CNT, ultimately resulting in the reduction of

Table IV The uses of CNTs in various biosensing fields

Area of application	Usage of CNT based biosensors	References
Enzyme reaction	By utilizing the electron transport chain in living organisms, the CNT-based electrodes can be used to monitor and catalyze the enzyme reactions	13
Antigen detection	Synthetically made antigens and aptamases can be coated onto the surface of the CNT electrode and can be injected into the body. When the particular antigen reaction takes place within the body, the color change or the electron release can be easily detected by the CNT electrode	13
Treatment of Autoimmune diseases	Many difficult autoimmune diseases can be temporarily treated by giving passive antibodies with CNT electrodes and proper monitoring processes	13
Pregnancy tests	Pregnancy tests can be easily done using anti-HCG hormone-coated CNT electrodes	13
Drug delivery	Certain cells open up channels when insulin is connected to the cell receptors. For insulin deficient people, insulin-coated CNT electrodes pave the way as a drug delivery agent	13
Customized dosage of medication	Using the responsive CNT electrode, the required dosage, concentration of certain drugs and the response to different cells can be plotted out. This is very useful in finding the right medicine for diseases	13
Glucose test	Glucose levels can be tested by CNTs in Si substrate functionalized with Ni nanoparticles	13
Eye treatment	CNT-based pressure sensors can be used to control the barometric pressure of the eye while handling fluids during a surgery	30
Medical inhalers	The dosage of inhalers can be controlled according to the body's requirement by monitoring with CNT-pressure sensors	30
DNA hybridization detection	A CNT-FET biosensor using a suspended CNT (SCNT) was developed to detect both single-stranded (ssDNA) and double-stranded DNA (dsDNA). dsDNA was found to weaken the conductance of the SCNT more than ssDNA	42
SARS-CoV-2 detection	A CNT-FET biosensor was developed by CNT printing to detect the SARS-CoV-2 S1 antigen from a fortified sample. The SARS-CoV-2 antibody was immobilized onto the CNT surface by 1-pyrenebutanoic acid succinimidyl ester (PBASE) in a non-covalent interaction. The biosensor showed higher sensitivity in less time (~2–3 min). This CNT-FET device could save a considerable amount of time with less clinical waste	43

time in $0' \rightarrow 1'$ state conversion of the entire device by two magnitudes.¹⁴

Vertically Aligned CNT-Based Data Storage

In a vertically aligned CNT-based data memory device, MWCNTs are vertically made to align with the source and drain electrodes by a precisely controlled CVD growth. The source is connected to the ground while the gate and drain are connected to the voltage supply (Fig. 8).¹⁴

When voltage is supplied, the drain and source of the CNTs are attracted to one another creating an electrical contact (conducting state $1'$). Now this electrical contact stays intact depending upon the length of the CNT; the longer the CNT, the steadier the contact. By using shorter and longer CNTs, volatile and non-volatile memory devices can be developed.¹⁴

Another advancement of this type is coating the source electrode with a dielectric SiN_x and metal Cr layer. These coatings change the source electrode to a CNT insulator metal (CIM) capacitor. This setup, when applying the voltage to the drain electrode, contacts the source and stores the charge in the CIM capacitor and vice versa. The dielectric coating could be changed for higher level storage systems.¹⁴

Suspended CNT-Based Data Storage Device

The NRAM device developed by Nantero Inc. is based on suspended CNT data storage. In this setup, the CNT is suspended between the source and drain while the gate is placed below the CNT with a gap. Van der Waals force is a key problem found in the cantilever CNT-based device, while in this setup the van der Waals force plays a very important role (Fig. 9).¹⁴

When voltage is introduced between the gate and the CNT, the van der Waals force is induced in the CNT by the oxide layer of the gate. Then the CNT and gate make an electrical contact (conducting state $1'$), and the device becomes non-volatile. A pull-out voltage should be applied to bring back the effect.¹⁴

The performance can be increased by decreasing the gap between the CNT and the gate, by increasing the length of the CNT and also by selecting a proper oxide layer. In this type, smaller diameter CNTs are selected and are placed at smaller gaps to reduce the time of transition from state $0'$ to $1'$.¹⁴

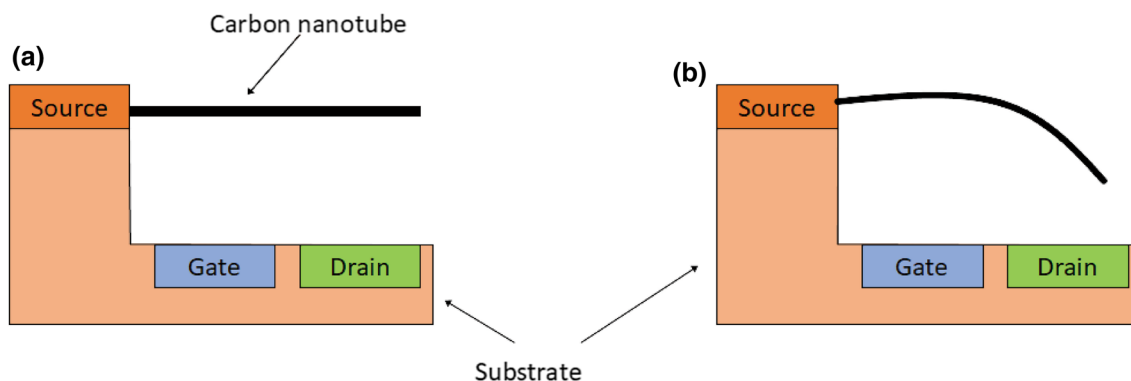


Fig. 7 Cantilevered CNT-based data storage device, (a) non-conducting state 0', (b) conducting state 1' (adapted from 14).

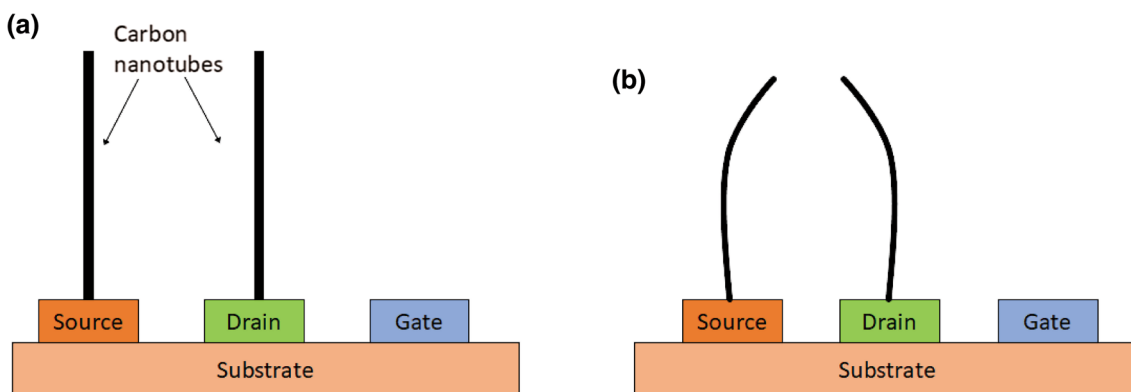


Fig. 8 Vertically aligned CNT data storage device, (a) non-conducting state 0' (b) conducting state 1' (adapted from 14).

Telescoping of CNT-Based Data Storage Device

The van der Waals force between the inner walls of a MWCNT plays an important role in this device setup. The source and drain are connected with open MWCNTs and separated by a nano-distance where the gate is placed (Fig. 10).¹⁴

When the voltage is applied, the inner walls of the MWCNTs from the source and drain slide off and connect with

each other in the gate resulting in a conducting state 1' (non-volatile memory). The conducting state 1' lasts depending upon the van der Waals force within the walls. DWCNTs can also be used for higher performance.¹⁴

Lithium-Ion Battery Application

Li-ion batteries are used as the source of energy in many electronic devices such as mobile phones, aeroplanes,

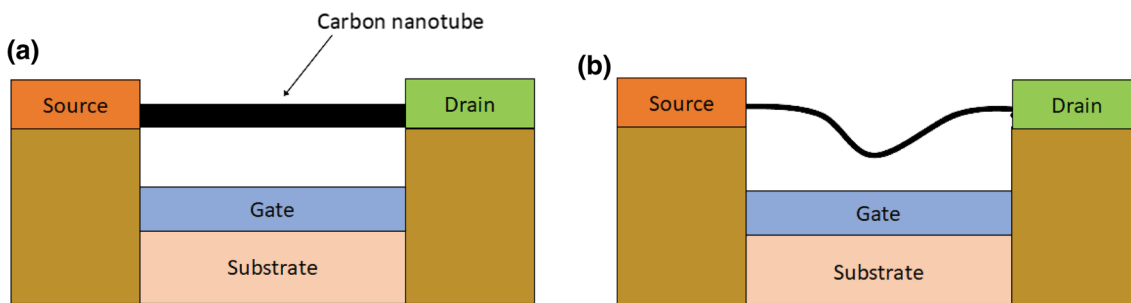


Fig. 9 Suspended CNT-based data storage device, (a) non-conducting state 0' (b) conducting state 1' (adapted from 14).

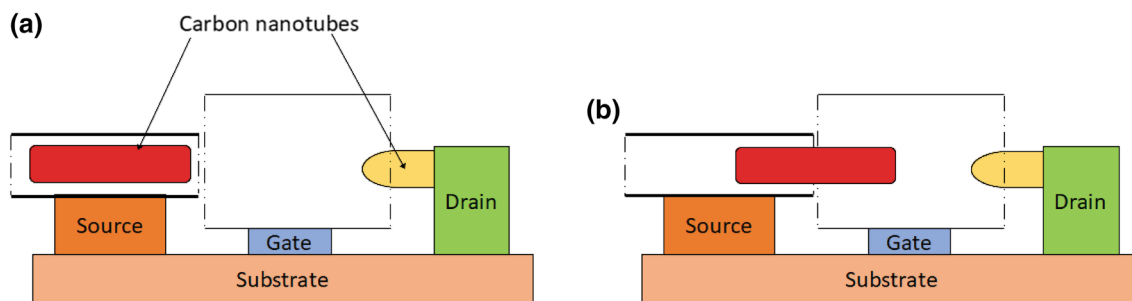


Fig. 10 Telescoping CNT-based memory cell, (a) non-conducting state 0' (b) conducting state 1' (adapted from 14).

lamps, medical equipment, and mobility devices. Commercial Li-ion batteries use graphite as their anode and lithium metal oxide as their cathode. In most batteries, Li ions undergo a specific type of storage called intercalation. Intercalation is where Li ions are stored without destroying their crystal structure, which increases the rate of ion exchange and also the lifespan of the battery. The Li ion migrate from the cathode to the anode during discharge and vice versa during charge.^{44,45}

Graphite has a C-C bond that is stronger than the van der Waals force between the sheets which causes the Li ion to be stored between them. But storing Li ions between the sheets creates swelling of the graphite sheets, ultimately leading to a limitation in the specific capacity (~372 mAh/g).⁴⁵ The replacement of the anode by a CNT, acid-treated CNT, CNT-based composites, and doped CNTs has many advantages in the overall performance and recyclability of the battery.^{44,45} CNTs have more locations for storing Li ions inside the cylindrical tube and electrochemically active sites on the outside. It is reported that after a Li ion enters a CNT, it can roam around freely inside the structure. This is why the length of the CNT plays a very important role in its diffusion coefficient. Shorter CNTs have higher specific capacity.⁴⁵

Both metallic and semiconductor CNTs have different Li insertion capacities. It is reported that metallic CNTs have 400% more insertion capacity than that of semiconducting CNTs. Molecular orbital methods were used to find the effect of CNT diameter on the absorption energy. CNTs with smaller diameter were found to give more preferred absorption.⁴⁵

Doping with boron helps in better Li-ion absorption by causing an electron deficient structure in CNTs; meanwhile, doping with nitrogen makes CNTs more electron-rich being retardant to Li-ion absorption.⁴⁵ An N-doped hollow CNT has been reported to give < 20% of fading in performance after 3500 cycles.⁴⁵ Ball milling is a proven treatment to increase the electrochemical performance of CNTs. Ball milling of thermal CVD grown MWCNTs show an approximate 54% increase in the reversible capacity and

51% decrease in irreversible capacity. Thus, the coulombic efficiency of the battery increases. One disadvantage of ball milling MWCNTs to improve performance is that it increases the voltage hysteresis of the battery by forming more functional groups on the surface of MWCNTs.⁴⁵

The graphene-winged CNT is a new structure in which graphene sheets are attached to the walls of MWCNTs in a wing-like manner. Graphene wings create defects in MWCNTs providing more Li-ion storage. A reasonable reversible capacity of 603 mAh/g after 2200 cycles was noted in anodes with graphene-winged CNTs.⁴⁵

Another treatment involves initially wetting MWCNTs with dimethyl formamide (DMF) and then suspending the mixture with 70 wt.% nitric acid.¹⁷ The acid treatment reduces the crystallinity, length and the impurities and enhances the sites for Li-ion storage.¹⁷ This also helps in increasing the reversible Li-ion storage in the battery.¹⁷ MWCNTs are more appropriate for battery applications than SWCNTs and DWCNTs due to their redox peaks. MWCNT batteries have redox peaks at low potential (0.15 V) while SWCNT and DWCNT batteries have redox peaks at comparatively high potential (1.2 V).⁴⁴

The performance of a CNT in a battery atmosphere depends upon its type, quality, manufacturing method, chirality and specific capacitance.⁴⁵ In commercial Li-ion batteries, a non-active copper current collector for the active materials. The copper collector is a dense material as it alone consumes nearly 10% of the whole cell weight while all active materials of the cell consume less than 55% of the cell weight. Replacing the copper collector with a lighter material is reported to improve the gravimetric performance of the battery. A study reports a CNT fabric used as an anode current collector which is lower in density, inexpensive, very thin and more flexible than copper making it a suitable alternative to copper collector. CNT fabric treated with isopropyl alcohol (IPA), when used as an anode current collecting material, saved 97% weight of the copper current collector. During the first cycle of charging, a small number of Li ions are lost in the process which is due to the irreversible capacity of the CNT. The Li ions are trapped in the

solid electrolyte interphase (SEI). This effect is detrimental to the overall battery performance,⁴⁶ so modifying a CNT in a way that it gives less irreversible capacity is beneficial for the battery.

TiO₂ is used along with a CNT and carbon fibre paper (CFP) to build a superior-performance battery in a report by Wang.⁴⁷ In this technique, a high-density uniform layer of CNT is grown on CFP using CVD. Then, 100 cycles of atomic layer deposition is used to coat amorphous TiO₂ over CNT/CFP. The effect of varied cycle number on the battery life is briefly studied by Wang.⁴⁷ TiO₂@100-CNT/CFP had an average diameter of 52 nm. Particularly, TiO₂@100-CNT/CFP showed a longer cycle stability. Also, as the specific capacity of the CNT/CFP electrode is small (~20 mAh/g), CNTs role in the irreversible capacity loss is almost negligible leading to better battery performance. This battery setup also records a 97% capacity retention after the 550th cycle. The surface-controlled capacitive process of TiO₂@100-CNT/CFP lithium storage helped to build a better battery.⁴⁷ Table V shows the varying capacities in different types of CNTs.

CNT-based composites such as CNT-Si, CNT-Sn, and CNT-Ge are also employed in Li-ion batteries.⁴⁵ Recently, LG Chem has invested around US\$53 million to expand the CNT production in their Yeosu plant in Korea. The entire EV (electric vehicle) market will run on CNT-Li-ion batteries by 2025, a prediction made by the US Department of Energy (Vehicle Technologies Office 2025).

Nanoelectromechanical Systems (NEMS)

To study at microscopic, submicroscopic and nanoscale levels, sensors of very small size are required. For a long time, microelectromechanical systems (MEMS) were used to analyse and record data on a small scale. Nanoelectromechanical

systems (NEMS) are devices integrated within ≤ 100 nm.⁴⁸ The replacement with CNT-based NEMS increases the robustness, lifetime and performance of the product. It is also helpful in reducing the energy consumption. It is found that the electric potential and strain of CNTs have a parabolic dependence. When SWCNT buckypaper (a thin sheet with aligned SWCNTs) is subjected to electric potential, it bends laterally showing a parabolic dependence on electric potential with only a 0.2% loss of strain after 140,000 uses.⁸ NEMS can be applied to many areas and some are mentioned below.

Nano Tweezers

The electromechanical response of CNTs paved the way for the construction of nano tweezers to aid in handling and investigating nanostructure elements. Nanotubes are attached to an electrode or a pre-determined substrate, and then a potential is applied to open and close the end caps of the nanotubes.⁸

A model of nano tweezers was developed by depositing MWCNTs in two different substrates as shown in Fig. 11. The opening of the MWCNT was controlled by macro-actuators attached to it and the closing was controlled by applying a certain electric potential.⁸ This particular model had a better grip on larger elements.⁸ Nano tweezers can be used in AFM (atomic force microscopy) for studying nanostructures.⁸

CNT-Based Nanosensors

A disadvantage of conventional sensors is that they are anisotropic, while CNT-based sensors are isotropic.³⁰ It is shown that CNT nanosensors have a higher order of magnitude of sensing than conventional solid-state sensors.³⁰

Table V The varying capacities in CNTs of different treatments in their first charge (C_{ic}) and discharge (C_{dc}); and their reversible (C_{rev}) and irreversible capacities (C_{irr})

Anode material	Capacity mAh/g				No. of cycles	References
	C_{ic}	C_{dc}	C_{irr}	C_{rev}		
MWCNTs by catalytic decomposition						45
(a) slightly graphitized	640	900	260	~ 400	20	
(b) highly graphitized	282	875	593	~ 200		
Thermal CVD grown MWCNTs						45
(a) purified	351	~ 1363	1012	311	50	
(b) purified + ball milled	641	~ 1159	518	616		
Free-standing and binder-free						45
(a) SWCNTs	2390	–	1691	~ 100	40	
(b) DWCNTs	2110	–	1730	~ 50		
(c) MWCNTs	750	–	262	~ 300		
CNTs prepared by spray pyrolysis						45
(a) long CNTs	188	615	427	142	20	
(b) grown short CNTs	502	1295	793	230		

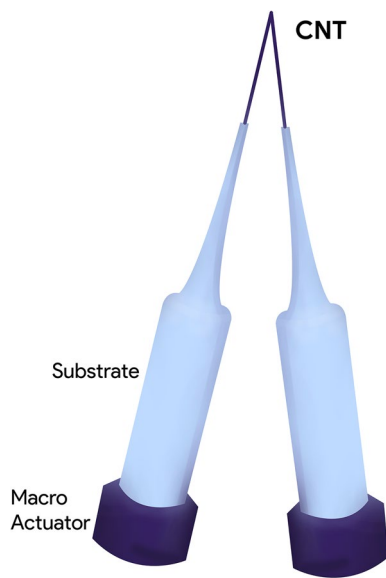


Fig. 11 A schematic model of nano tweezers (adapted from 8).

CNT sensors are smaller in dimension and also have a large surface area and comparatively higher conductivity (electrical and thermal) than conventional sensors.⁸ Certain arm-chair SWCNTs have the ability to transform from metallic conduction to semiconduction under pressure, and there is reportedly a linear relationship between the potential difference and strain in pressurized SWCNT films.³⁰ SWCNTs also show a reversible piezoelectric effect under pressure.³⁰ When MWCNTs are examined for applications in sensors, they resulted in μW power consumption with the possibility of ultra-low energy consuming sensors.³⁰

Pressure sensor: When pressure is applied to SWCNTs using a diamond anvil cell, there is a shift in the D^* band (2610 cm^{-1}) of the Raman spectrum, and the shift reversed when the pressure is released.⁴⁸ This property of the SWCNT can be used to detect pressure in various fields. Pressure sensors are used to control the pressure of nozzles in plant fertilizer systems.⁴⁸ A piezo-resistive pressure sensor, that is, a sensor which changes its electrical resistivity with respect to the strain applied, was developed by growing SWCNTs in polysilicon. When air pressure is applied, a uniform change in resistance is reported, and the process reverses when the pressure is removed.³⁰ MWCNTs, when heated, detect argon and nitrogen gases at different pressures;⁴⁹ this property can be used to build a pressure sensor inside a gas-filled vacuum tube.

Flow sensor: It is reported that the electric potential and fluid flow velocity of a CNT sensor have a linear dependence.⁴⁸ Voltage saturation is found to occur at flow velocity around 10^{-5} m/s .⁴⁸ A flow sensor was developed with a bundle of SWCNTs, which is placed within two electrodes.

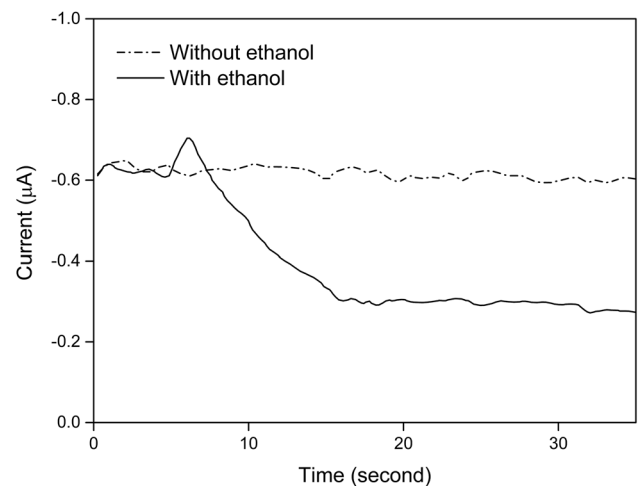


Fig. 12 Drain current with respect to time for a gate bias of -10 V and a source bias of -100 mV (reprinted with permission from 30, Someya et al., Nano Lett. 3, 877 (2003).© 2003, American Chemical Society).

This sensor setup has a direct signal because of the polarity of the water molecules.³⁰

Acoustic sensor: CNT-coated surface acoustic wave (SAW) sensors have higher sensitivity than normal SAW sensors.³⁰

Gas sensor: When a gas sensor using a single SWCNT between gold electrodes is built and tested, the electrical conductivity for vapors of NO_2 and NH_3 changes by several orders of magnitude. The conductivity increases by three orders of magnitude for 200 ppm of NO_2 within 10 s but conductivity decreases by two orders of magnitude when exposed to 1% NH_3 for 2 min. This fluctuation in electric conduction is because when NO_2 reacts with the SWCNT, it withdraws an electron, while NH_3 donates an electron to the SWCNT.⁴⁸ Gas sensors made of SWCNTs and a palladium-modified SWCNT can detect hydrogen gas in a temperature range of 25°C to 170°C .³⁰ Two innovative approaches to gas sensing are given below.

(i) **CNT-composite gas sensors:** Composites with CNTs are also used to build sensors; for example, a MWCNT- SiO_2 composite was constructed to detect gases of different types and in closed spaces.³⁰ A CNT-PMMA (poly(methyl methacrylate)) composite sensor is found to sense organic ethyl acetate vapors at 30 orders of magnitude.³⁰

(ii) **CNT-FET alcohol sensor:** A unique SWCNT-FET-based sensor was developed to detect vapors of alcohol, as SWCNT-FET shows a spike in the drain current when ethanol is passed through its surface.³⁰ The plot of drain current with time is given in Fig. 12.

Nano-switches

Electromechanical switches with good reproducibility, faster switching time and high operating frequency can be produced by building CNT-based nano-switches.⁸ The mechanism and design of nano-switches is similar to the data storage devices mentioned in section 4.3. There are four types of three-terminal switches built using CNTs, which are suspended, vertical, telescoping and cantilevered.⁸ For all types, the working mechanism is the same.

1. The electrodes are deposited or etched onto the source, drain and gate
2. Positive voltage is applied across the source electrode and negative voltage is applied to the gate (or drain) electrode
3. The CNT starts to deflect towards the gate (or) drain electrode
4. After a threshold voltage, the CNT comes into contact with the gate (or drain) electrode, which is called the ON switch V. Then a pull-out voltage is applied and the CNT reflects back to the original form going to the OFF switch.⁸

Other Applications

There are several other electronic applications in which CNTs are tested for replacement.

Lamps: Field emission lamps (FEL) require high efficiency at low power.⁵⁰ By using a metal mesh as the gate electrode, CNT-based FEL are designed by screen-printing resulting in stable and steady CNT lamps. The vibration of the metal mesh can be significantly decreased in this design.⁵⁰ Nanotube-based lamps are reported to have a lifetime of 8000 h.⁹

Supercapacitors: The volumetric specific capacitance of a block of CNT is 107 F/cm³.⁷ The highly porous structure makes them suitable for the construction of supercapacitors. A CNT-RuO₂·xH₂O composite electrode was built and then annealed and pressed to remove any impurities and defects.⁷ When 55–75% of RuO₂·xH₂O is present, the capacitance is reportedly around 720 F/g.⁷ Thus, CNT-based supercapacitors do better in high-power applications.⁷

X-ray: CNTs can also be used to produce X-rays by focusing a CNT cathode against a metal-coated anode.⁹ X-ray machines with high efficiency, portability, and less power consumption can be built using CNTs.

Welding: For nano-spot welding, a strong and cost-effective design is built by using CNTs. CNTs are filled with copper solder and when a potential is applied, a solder flow rate of 120 ag/s is observed. This setup required only a few volts to initiate Cu migration.⁵¹ A filler rod is made of a

1 wt.% CNT-AZ31 magnesium composite by ball milling. Ball milling gives a uniform distribution of CNTs in magnesium flakes. When the filler rod was used in gas tungsten arc welding along with argon gas to prevent atmospheric contamination, it resulted in increased tensile strength of the weld and also had a hardness of 67±3.6 which is greater than the non-reinforced weld of AZ31 magnesium (53±4.5).⁵²

Diodes: In the semiconducting industry, the conventional p-n junction diodes are expected to be replaced by CNT diodes very soon. CNT-based diodes are built by contacting two nanotubes of different diameters from end to end creating a Schottky barrier connection.⁵¹

Emerging applications: In 2018, NASA revealed that they are studying carbon nanotubes for mini electron probes to be used in space to measure the chemical properties of objects in vacuum. CNT composites can be used as antistatic shields in future vehicles to reduce electric discharge.⁶ CNT-based photovoltaics are also under study in laboratories. Many other fields such as textiles, dyes, water purification, paints, instrumentation, and gas transport can also gain advantages by using CNTs in their products.^{11,18}

Conclusion

Electronics, as a growing industry, demands more miniaturization. This miniaturization of electronic products has many benefits, such as easier portability, minimum use of raw materials, low power usage and less e-waste. The amount of research on CNTs has quadrupled since 2010. Soon, it is likely that CNT-based electronics will be used to produce affordable, miniature and powerful electronic products. This paper reviewed several approaches using CNT in electronic products, such as in field emission transistors, data storage devices, energy storage batteries and more. CNT performed well in most all the applications that were reviewed. The large-scale production of CNT is still a question to answer before implementing CNT electronics. Even if we have found the right technique to produce CNT economically, controlling the growth of nanotubes and the number of impurities are some important parameters to be considered for producing CNT. Another important parameter to consider is the biocompatibility of CNT in our ecosystem. As CNTs are very small, they may easily escape into the atmosphere and can even cause health problems if inhaled by humans.⁵³ A study by Lam⁵⁴ revealed that SWCNTs caused lung inflammation in the form of interstitial granulomas and the inflammation was dosage-dependent. But studies by Aoki⁵⁵ showed that MWCNTs cause less toxicity as “tattoo ink”. Very few studies have been done on the compatibility of the material. If CNTs are approved to be safe in all aspects, inventing devices at nano-level has no limits.

Conflict of interest The authors declare that they have no conflict of interest.

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