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Carbon Nanotubes: Factors Constituting The Development Of Nanotechnology

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Abstract

Carbon nanotubes' (CNTs) has become the building blocks of nano technology for energy system development, because of its astonished mechanical, energy storage and unique electronic properties. These ensure its relevancy for applications in enormous areas presently and in the future. Areas of applications include field emission devices, high-strength composition, sensors, nano-biomedicals, nano-systems, nano energy storage system and other related fields. This report reviewed CNTs' properties and how they are related to their physical and chemical structure. The design criteria for this material were critically reviewed which includes manufacture and cost savings. The growth of carbon nanotubes and manufacturing to its appropriate form such as purification, characterization and functionalization were comprehensively revised and reported. The current and future areas of applications of CNTs were identified; examples are nanoelectronics, scanning nano-microscopy, biomedical sensors, nano energy storage system etc. This report is concluded with the progress made so far since CNTs were discovered and the potential challenges, potential solutions and it significant for meeting future energy needs among others.

Keywords: Carbon Nanotubes, CNTs, energy storage, design consideration, applications

Introduction

Carbon nanotubes (CNTs) is an exciting field of study in the emerging nanoscience and nanotechnology.[1-8] Nanoscience and nanotechnology has ubiquitous applications in medicine, energy, education, transportation, agriculture, communication, etc summarized in the Figure 1 below. This review presents some researches in this field of carbon nanotubes (CNT) and potential applications.

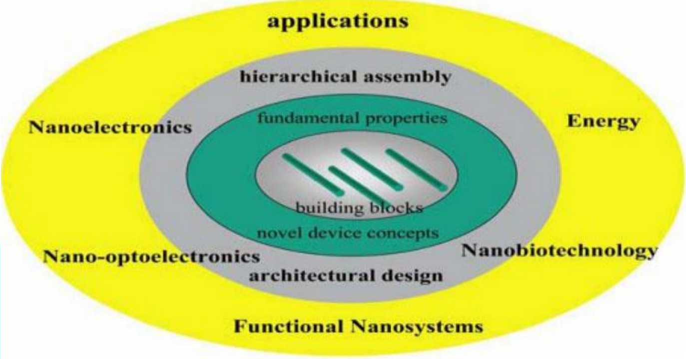

Figure 1. Overview of nanoscience and nanotechnology applications. [2]

Carbon nanotubes

Carbon nanotubes (CNTs) are novel materials in materials science and engineering that was first discovered and extended to fullerenes by Sumio Iijima in 1991. [9] The discovery of CNTs then ignited research on growth, characterization, application and development, which has exploded due to the amazing electronics and extraordinary mechanical properties of CNTs.[10] Thus CNT can be conducting, and hence provides the potential to create semiconductor to semiconductor and semiconductor to metal junctions, useful in electronics device.[8-9] The high-tensile strength and Young's Modulus, and other mechanical properties provide assurance for high-strength composites for structures application.[10] This compliments the prediction of [11] the revolutionary design concept in future aerospace vehicles will basically rely on novel materials with extraordinary structure properties to enable significant reduction of mass and size of components, while imparting intelligence. The combination of the unique electronics and extraordinary mechanical properties of carbon nanotubes (CNTs) are expected to allow this paradigm shift in design concepts.[1-4.] ·Again, the significant challenge of translating these CNT properties into macrostructures for future aerospace vehicles is acknowledged. [11] However, the methodology to assemble nanostructures to useful macrostructures is not yet imminent. [11] Hence, optimization was expressed by established facts that researchers exploring CNTs has been making some significant progress for the past decade by joining carbon nanotubes into conventional materials in broad areas of applications[12] as in nanoelectronics, sensors, field-emission base displays, batteries, polymer matrix composites, re-enforce materials, electrodes, heat and biomedical sensors etc. [2, 4] The exploration of CNTs is inexhaustible as at this time because continuous research and critical analysis of the extraordinary electrical and mechanical properties have shown their potentials for useful application in new areas such as efficient energy usage, photovoltaics, piezoelectric nanogenerators, amongst others. [12]

Structure and properties

Basically, there are two chemical structures of CNTs with the same properties; the first is single-walled carbon nanotubes (SWCNT) and other multi-walled Carbon nanotubes (MWCNT).[4,10-11] Both are interesting nanomaterials for obvious reasons, for example CNTs can either be metallic or semiconducting, depending on its chiral vector (n, m) where n and m are two integers. [10]

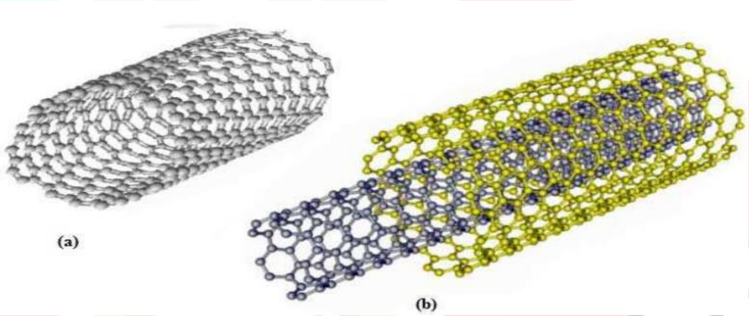

Figure 2. Schematic of a SWCNT (a) and a MWCNT (b) [13]

Carbon nanotubes can be synthesized in two structural forms single-walled and multi-. [9,13-14] The single-walled CNT (SWCNT) can be best described as a rolled-up tubular shell of graphitic sheet as shown in Figure 2 which is capped at both ends by half dome-shaped half-fullerene molecules with a diameter of 1 nm which are made of benzene-type hexagonal rings of carbon atoms.[10] The multi-walled CNT (MWCNT) is a rolled-up stack sheet in graphitic and concentric cylinders, with the ends either capped by half fullerenes or kept open. [10] An arrangement (*n*,*m*) used to identify each SWCNT refers to integer indices of two graphene unit pattern vector corresponding to chiral vector for nanotubes. [10, 14]

Furthermore, nanotubes are described by using one of the three morphologies; armchair, zigzag and chiral. [10-13] Here, Figure 3 shows the assembly of the carbon hexagon of the graphitic sheet with distinct chiral vectors and angles. [10, 13] The indices of the vector determine the morphology of the nanotubes as elsewhere reported. [13]

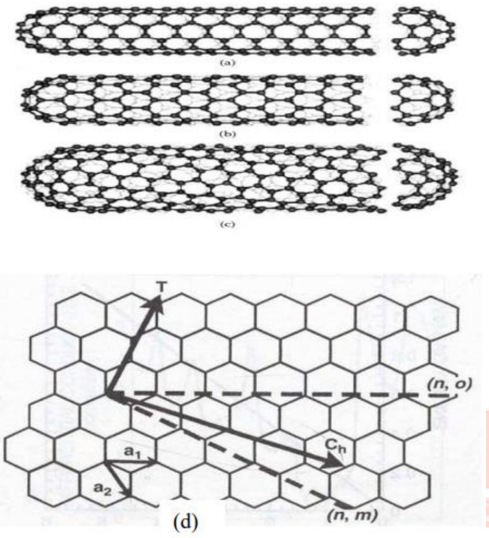

Figure 3. Schematic of nanotube morphologies: (a) armchair, (b) zig zag, (c) chiral, (d) structure orientation and properties. [13]

Some properties of CNTs were reviewed describing the morphologies of nanotubes structures and presented nanotubes types of (*n,m*), shown in Figure 3(b) are commonly called armchair because of their shape, perpendicular to the tube axis and a symmetry along the axis of short unit cell (*0.25nm*) that can be repeated to make the entire section of long nanotubes.[15-16] The nanotubes type (*n,0*) are known as the zigzag nanotubes shown in the Figure 3(c) because of the zigzag shape perpendicular to the axis, and they also have a short unit cell (*0.43 nm*) along their axes. Srivastava et al argued that the variance of morphology of the nanotubes can lead to change of the properties of the nanotubes; citing an example, the electronic properties of an armchair are metallic. [16] On the other hand, the electric properties of the zigzag nanotubes are semiconducting. [16] Lau and Hui reported that nanotube structural morphologies were determined based on a mathematical model developed using the chiral vector indices .[17]

Most CNT researchers such as Iijima, Mayyappan, and Siegel have reaffirmed about the extraordinary combination of physical properties that carbon nanotubes possess. Thus, curiosity to investigate the physical properties of carbon nanotubes has been determined by research conducted both experimentally and theoretically. Initially, researchers adapted the use of vibration of nanotubes as a function of temperature to calculate the Young's modulus of 1Tpa .[18] In addition, Figure 4 shows the high strength of CNT as compared to other engineering materials, thus led to prominent interest in carbon nanotube embedded materials. [19]

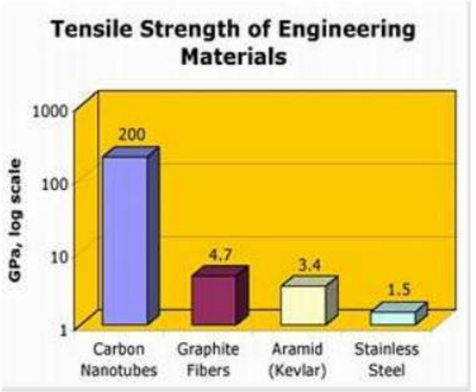

Figure 4. Chart comparing SWCNTs with other common high tensile Materials. [19]

Furthermore, methods commonly used to measure elastic properties of individual carbon nanotubes include the micro Raman spectroscope [20], thermal oscillation by transmission microscope [18,21] and application of force on a nanotube rope suspended across a pit using an atomic force microscope cantilever [18, 22]. Pan et al. [23] identified also other groups of researchers that performed tensile test experiments of the CNTs rope properties and obtained an average value for each tube based on the numbers of nanotubes on the rope. The experimental values measured have produced tensile modulus and strength values for single-walled (SWCNTs) and multi-wall CNTs (MWCNTs) ranging from 270Gpa to 1Tpa and 11Gpa to 200Gpa respectively. [17]

Single and multi-walled nanotubes have very good elastic and mechanical properties because the 2-D lattice carbon atoms in a graphitic sheet allow a large amount of plane distortion. The structural and material characteristics of carbon nanotubes suggest their possible use of making lightweight but highly elastic and very strong composite material. [12] In addition, Doudero and Gorga [13] emphasize light weight CNTs pointing at their hollow, tubular and caged molecules. CNTs have been proposed for lightweight, large-surface-area packing materials for gas storage and hydrogen storage devices, gas and filtration devices, nanoscale container for molecules drug delivery and casting structures for making nanowires and nano-capsulates among others. 12, 13

In complement to the mechanical properties of CNTs, researchers have examined the thermal conductivity and electrical properties with modeling used to determine the conductivity via the structure of nanotubes as compared with graphite.

Conductivity is largely dependent on the small variation of nanotubes, as established based on mostly theoretical work done. [24] For instance, Brett et al. [25] founded unusually high thermal conductance of 6000W/m K at room temperature for a single nanotube structure using non-equilibrium and equilibrium molecule dynamics. In similar fashion, for electrical conductivity, experimental four-probe measurement of individual nanotube structure reported resistances in the range of 5.1 $x10^{-6}$ – 5.8Ω cm (Conductivities range from 0.17 to 197,078S/cm). [24]

In addition, Meyyappan and Srivastave [12] equally recognize that nanotubes are high aspect –ratio structure with good electrical and mechanical properties, thus, the application of nanotubes in field emission display, scanning probe microscope tips for metrology and other areas has started to materialize in the commercial sector.

Design consideration of producing CNTs

An extensive literature of the laboratory-scale reported synthetic techniques including growth, mechanism, and purification for carbon nanotubes and the details design for both the (CNT-PFR) and (CNT-FBR) processes.[26]

Fundamentals of engineering design principles as well as materials properties are area needs to be considered for design criteria for industrial-scale production processes for carbon nanotubes. The design criteria may include, process operating conditions such as process temperature, pressure, coolant flow rate, reactors types and dimension. Energy requirement, currents, voltage, electrode diameter and graphite evaporation flow rate are also critical in synthetic techniques. [25-26] Furthermore, design studies include carrier gas, reactant, product, catalyst, nanotubes yield and selectivity, conversion and purification. 26

Other design considerations include capital and cost of operation, raw materials selection, manufacturing process (semi-batch, batch or continuous), production and purification method.[25-26] The process operating conditions, such as temperature, pressure, catalyst performance, high product yield, reactants conversion and selectivity must be equally considered.[26] Criterion such as process operation conditions will be importantly considered for the design because cost of operation and energy requirements can be reduced if the operating pressure and temperature is kept low as possible. [26].The deactivation time and regeneration method which are activities of the Catalyst performance, determined the extent of the reaction and as well as process selectivity of the desired product were adequately reported.[26]

The design consideration of CNTs product was clearly articulated in the conceptual design.[26]
Two industrial -scale synthesis techniques for conceptual design for carbon nanotubes industrial scale production using one, the HiPCO reactor and the other CoMoCAT reactor were presented.[26] Major design factors considered are low cost of production, high product yield and selectivity, catalyst performance, moderate pressure and operation temperature. "*The capacity of the conceptual design was 5000 metrics tons/year which is the size of carbon nanofiber plant operated by Grafil, a California based Mitsubishi Rayon subsidiary*", furthermore "*carbon nanotubes will displace carbon fiber in advance polymer composites, and the plant capacity is comparable to any carbon fiber facilities*" according to Agboola et al. [26].

Design consideration for using CNTs

CNTs are nanoscale materials. [2, 9-10] It is apparently becoming significant advantage for dimensional circuitry for electronics engineer stepping in micro-scale. [27] Design must be at nanoscale not microscale.[27] Therefore, the size of CNTs and how to assemble or physically modify during usage it's an important thing to be considered, because it is still very challenging to use the absolute precise and quality equipment used in micro manufacturing for nano manufacturing.[27] The size and length of carbon nanotubes must be highly considered for usage.

Production and manufacturing

There are three main method of producing carbon nanotubes includes direct-current arc, Laser ablation and chemical vapor deposition (CVD). The first approach use to produce carbon nanotubes was the direct-current arc method [28] but pioneered by Ijiima. [14] Then shortly followed by Laser ablation which was developed by Rice University [10], thereafter CVD and other related technique became available for carbon nanotubes production processes. The figure in metric for an ideal production processes depends on the application. These processes are described briefly below.

However, Agboola [26] argued that these three methods of production of carbon nanotubes are basically for laboratory scale and tactically developed a conceptual design of carbon nanotubes processes which appears to be feasible for industrial-scale production of CNTs with comparative economic market price with that for the market price of carbon fibers. [15, 26] Taking into consideration the design concept of Agboola, two laboratory-scale catalytic chemical vapor deposition reactors were selected: One (CNT-PFR process) used the high pressure carbon monoxide disproportional reaction iron over catalytic particle clusters (HiPOC reactor), and the other (CNT-FBR process) used catalytic disproportional carbon monoxide over a silica supported cobalt-molybdenum catalyst (CoMoCAT reactor) used in design plant for industrial scale production. [26] The market analysis of CNTs product and application for industrial and domestic processes are systematically presented.[15]

Arc process and Laser Ablation

Carbon nanotubes production using direct arc process involves striking a DC discharge in a gas inert (such argon or helium) between a set of graphite electrodes. [9, 10, 28] This act courses vapors from the electric arc to hollow graphite anode pack with mixtures of transition metal (such Fe, Co or Ni) graphite power. 60 to 600 torr maintained for the inert gas flow, nominal conditions involve 2000 to 3000^{o}C at 100A, and 20V, thus produces SWCNTs and with a mixture of MWCNTs and soot. [10] To change the yield of the nanotubes the gas pressure, flow rate and metal concentration can be varied. However, these parameters do not have any significant change to the diameter distribution. The typical diameter distribution of SWCNTs by this process seems to be 0.7 to 2nm. [10] Detail of this production process of CNTs can be seen are reported. [9, 10, 28]

Laser Ablation

The second production method known as laser Ablation process involves a target consisting of graphite mixture with small amount of transition–metal particles as catalyst placed at the end of a quartz tube enclosed in a furnace.[10, 16, 29] The target is exposed to an argon ion laser beam that vaporizes graphite and nucleates CNTs in the stock wave just in the font of target.[10] The reactor, in which the argon flows through, is heated to 1200^{o}C by the furnace carries the vapor and nucleated nanotubes and continues to grow. [26] The nanotubes are deposited in the cooler walls of the quartz tubes downstream of the furnace. Thus, produces a high percentage of SWCNTs of about (~70%) with the rest being catalyst particles and dust. [10]

Chemical vapor deposition (CVD)

Thirdly, this CVD technique involves the use of energy source such as plasma, a resistive or inductive heater, or a furnace transfer energy to a gas-phase carbon molecules over metal Catalyst deposited substrates to produces fullerenes, carbon nanotubes, and others like nanostructures. [10, 27] Carbon monoxide and hydrocarbon feedback such as methane, acetylene, ethylene and x-hexane are the commonly gaseous carbon sources used. The CVD can be used to preferably to synthesize multi wall carbon nanotubes depending on the option of suitable metal catalyst. Carbon nanotubes growth by the template based chemical vapor technique demonstrates very good alignments and positional control on a nanometer scale. [10, 27] The size of the nanotubes is determined by the size of the particles and pores, and can be controlled, prior to the carbon deposition. This is achieved by regulating the amount of the feed stock supplied and the thickness of the membranes, thus the length of the carbon nanotubes can be controlled. [30]

Chemical vapor deposition synthesis technique can be classified according to the energy source, such as thermal chemical vapor deposition and plasma enhanced chemical vapor deposition (PECVD). [10, 30] These two chemical vapor deposition synthesis techniques are apparently the conventional techniques used to grow carbon nanotubes. These thermal chemical vapor deposition and the PECVD are detailed in other reviews.[10, 26, 31] Other chemical vapor deposition synthesis techniques is also extensively reported [27], including conceptual design: One (CNT-PFR process) used the high pressure carbon monoxide disproportional reaction iron over catalytic particle clusters (HiPOC reactor), and the other (CNT-FBR process) used catalytic disproportional carbon monoxide over a silica supported cobalt- molybdenum catalyst (CoMoCAT reactor). [26] The following figures show some of the CVDs growth processes of carbon nanotubes.

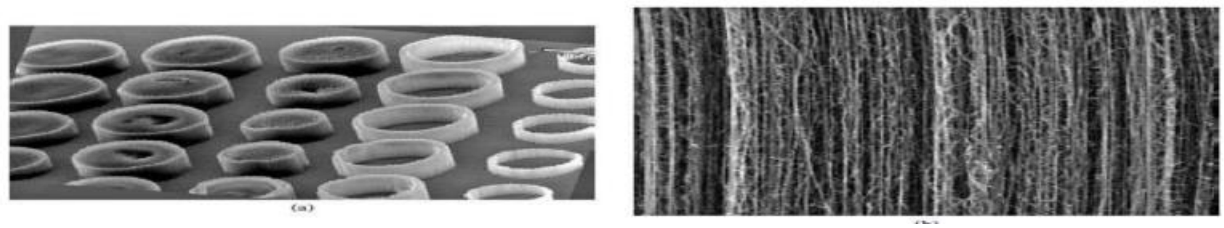

Figure 5. MWCNTs grown by thermal CVD: (a) Different catalyst solution concentrations results in tower sand ring-like structures. (b) Close-up view of one of these structures in (a) showing forest of nanotubes supporting each other by VDW force, thus resulting in a vertical structure. [12]

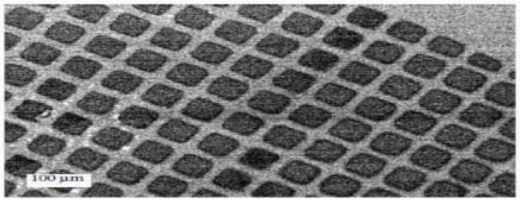

Figure 6. SWCNTs grown by thermal CVD on a 400 mesh TEM grid. [12]

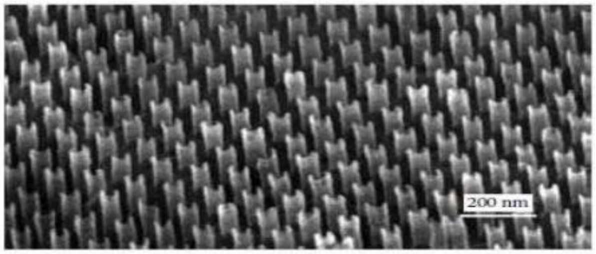

Figure 7. An ordered array of MWCNTs grown using an alumina template. [12]

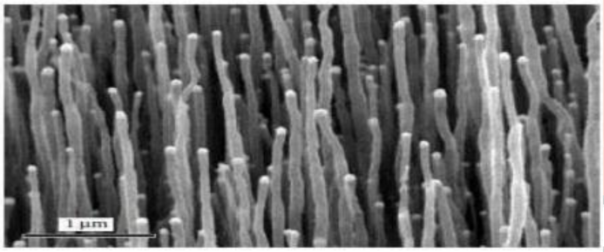

Figure 8. Vertically aligned CNFs from a DC plasma-enhanced CVD processes. [12]

Material development

The following process involves the development of the carbon nanotube manufacturing into appropriate forms:

Purification

The purification process of carbon nanotubes has been developed to remove all forms of impurities for the material. [12] Typically, as grown materials contains mixtures of SWCNTs, MWCNTs, amorphous carbon, graphite and catalyst metals particles, the ratio of impurities varies from process to process and largely depends on the growth (production) condition of a given process. [12] The purpose is to remove all form of impurities from the carbon nanotubes before they can be used for applications such as composite, nanoelectronic, nanobiomedicals, battery fuel cell etc. The need to improve the quality and yield of the carbon nanotubes made purification essentially important, and these methods includes oxidation, acid treatments, annealing, microfiltration, ultrasonication, ferromagnetic separation, and functionalization and chromatography techniques. [12]

However, it was acknowledged that, different purification techniques can be combined two or more methods. [27] For example, an initial mild oxidation were used to removed amorphous carbon and expose catalyst metals particle surface, then it was followed by treatment in strong acid to dissolve the catalyst particles or treatment by an organic solvents to dissolves fullerenes. [27] High temperature of (800 – 1,200 ^{o} C) is used to dry the carbon nanotubes produced. The structural surface of the CNTs can be altered from the purification technique employed, and caution must be taken into account when adapting purification methods. Thus, purification should remove carbonates graphite impurities and catalyst metals particle without insignificant impact to the carbon nanotubes material. [30]

Characterizations

Carbon nanotubes characterization have been developed for the purpose to obtain valuable information from the nanotubes structure in terms of dimension, open vs. closed ends, amount of amorphous materials present and defects and nanotubes quality. This process is facilitated by using high resolution TEM. [12] In MWCNTs, the spacing between layer is 0.34nm and, thus a count to the numbers of the walls is readily provides the diameter of the structure. [12, 26] It appears to be critical to determining the nanotubes-growth characterization because of the nature of catalyst and size of particle distributions. [12] But researchers have used the TEM, EDX and FAM to characterize the catalyst surface earlier to loading the growth reactor. [12, 32] Information of the particle size and composition of the surface can be obtained by the use of these techniques together. [32]
The Raman spectroscopy was presented in [35], which is another carbon nanotubes characterization techniques used besides the TEM. It is probably the most characterization technique used to study carbon nanotubes. [32, 35] Raman spectroscopy of the SWCNTs is a resonant process associated with optical transition between spikes in the 1-D electronic density of states. [32] The diameter and metallic against semiconducting nature of the SWCNTs is dictated and the energy of the allowed optical transition, thus this characterization is used to determine the diameter and the nature of the carbon nanotubes. [32] For example, Figure 9 shows a typical characteristic Raman spectrum with a narrow G band at 1590 cm^{-1} and the signature band 1730 cm^{-1} of the SWCNTs. [35] A strong enhancement in low frequency is also observed in the low frequency region for the radical breathing mode (RBM). [35]

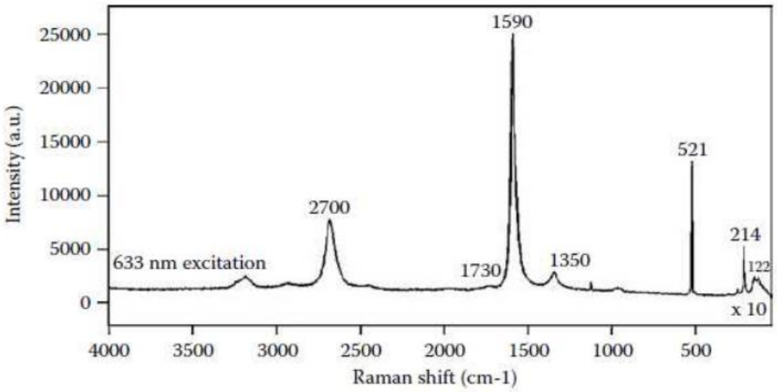

Figure. The Raman spectra of CVD growth SWCNT sample. [35]

Functionalization

Functionalization of carbon nanotubes modifies the properties for a particular application on the sidewall using other chemical groups. [10, 12, 34] For instance, the sidewall of CNT can be improved for atomic bonding or adhesion characteristics of carbon nanotubes in a host of polymer matrix to make functional composites with chemical modifications *"Functionalization of nanotubes ends can lead to useful chemical sensors and biosensor"* according to Mayyanpan et al. [12]

Reaction of soluble SWCNTs with dichlorocarbene led to functionalization of nanotubes with Cl on the sidewall. Carbon atom in SWCNTs of 2% saturation with C- Cl is sufficient to lead to rapid changes in the electronics band structure. [34]

Current and future applications of carbon nanotubes

Current and future applications of carbon nanotubes have been mentioned in various sections of this research as a novel material. This section formally recognizing areas were CNTs applications are significant. The extraordinary electronics, thermal and mechanical properties [12] has made carbon nanotubes widely applicable in nanoelectronic, field emission [12], biological/chemical & detection, digital electronics & computing [2], photonic. [1] CNT base scanning probe microscopy [25], energy storage devices, CNT base medical; production of computed tomography, x-ray and magnetic resonance imaging [36] just to mention a few. These areas of application mentioned has been successfully applied and more progress is still been made in ensuring cost effectiveness and other significant benefits for CNTs applications .[36]

Future applications of carbon nanotubes is vast according to notable researchers like Agboola, Iijima, Lieber , Mayyanpan amongst others, who have identified some feasible application areas and serious research is ongoing to ensuring realization. Future CNTs nano-systems application include: three-dimensional nano-processing systems, hybrid digital-biological processors, spin and quantum-based electronics [1], lightweight aerospace vehicle [11] and bio-medicals. [36] Currently, carbon nanotubes research is intensified in energy generation and storage applications.

Carbon nanotubes and energy

Presently, carbon nanotubes are making significant progress in energy efficiency and storage. In fact, using CNTs for energy applications is becoming more attractive to research because of the high demand of global energy requirement and it amazing chemical, thermal properties and electronic properties. According to Michael Arnol [37] stated that *"We've made a really fundamental key step in demonstrating that it will be possible to use these new carbon nanotube materials for solar cells one day,"* this new invention is an attempt to challenge silicon as the predominant photovoltaic cell materials. This has shown the possibility of carbon nanotubes to absorb and convert energy from the sun. [37]

Another application of carbon nanotube for energy storage is Electrochemical Capacitors. Carbon nanotubes have been found to be effective in electrochemical capacitors because it possessed good chemical stability, conductivity, and large surface area. [38]

Carbon Nanotubes as Photo switching Energy Storage Units

Also, it's discovered that carbon nanotubes could help us store and use solar energy even after the sunset. [37] Scientists at MIT and Harvard have designed a prototype system with capability to store solar energy through photo switching molecules; the energy stored can later be used in homes for cooking or heating purposes. [38] Azobenzene which is known as the organic compound for photo switching is a decent example of photo switching molecule; it is attached to substrates of carbon nanotubes. [38] These molecules can absorb the sun as energy, store it stably and indefinitely, and then discharge on demand. [38] The solar energy storage system could be considered as a further testimony of the realization of nano-energy technological advancements. According to Kumar [38] "*Researchers continue to search for more ways to use carbon nanotubes for the storage and enhanced utilization of existing products and designing and developing novel creations that can be used to meet energy needs".*

Conclusion

Carbon nanotubes are promising state-of-art material. It has shown significant level of progress in the past decades on the development of their extraordinary mechanical, energy storage and unique electronic properties. The use for state-of-the-art applications such as biomedical sensors, visual aids devices, electronics devices and the advancement of lightweight aerospace vehicle technology, solar energy storage system among others cannot be over emphasized. This novel material is faced with some major challenges; firstly, the manner in which carbon nanotubes can be produced from micro-scale to industrial-scale quantities still suffers from some set-backs. Secondly the syntheses and functional characterization of carbon nanotubes are still carried out within laboratory capabilities, thus limiting the ability for potential industrial-scale produce and manufacturing. Thirdly, lack of raw materials is a significant issue which affects the capability for mass productions of CNTs. However, major breakthrough of these concise areas will effectively increase current and future applications and cost effectiveness of structural and energy applications, thus the popularity of carbon nanotubes.

It is not out of place to mention at this point in time that carbon nanotubes could become a vital source of alternative energy in present and future energy needs because of the uncertain future of fossil fuel. Finite innovations recorded in the area of energy storage applications and its utilization gives a strong indication of this hypothesis.

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