

# Potential Applications of Carbon Nanotubes

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**Abstract.** This review explores the state-of-the-art applications of various kinds of carbon nanotubes. We will address the uniqueness of nanotubes that makes them better than their competitors for specific applications. We will discuss several examples of the already existing commercial uses of nanotubes and then point out feasible nanotube applications for the near term (within ten years) and the long term (beyond ten years). In our discussions of the applications, we will distinguish between the various kinds of nanotubes in play today, ranging from multiwall nanotubes having different degrees of perfection to the near-perfect molecular single-wall nanotubes. The last decade of research in this field points to several possible applications for these materials; electronic devices and interconnects, field emission devices, electrochemical devices, such as supercapacitors and batteries, nanoscale sensors, electromechanical actuators, separation membranes, filled polymer composites, and drug-delivery systems are some of the possible applications that have been demonstrated in the laboratories. We further discuss the status of this field and point out the value-added applications that exist today versus the revolutionary applications that will ensue in the distant future. The opportunities, challenges and the major bottlenecks, including large-scale manufacturing for nanotube material, will be identified as we define the applications space for nanotubes. We will also consider some of the recent concerns regarding health, environment as well as handling and safety protocols for carbon nanotubes.

## 1 Introduction

The combination of structure, topology, and dimensions creates a host of physical properties in carbon nanotubes that are unparalleled by most known materials. After a decade and a half of research efforts, these tiny quasi-one-dimensional structures show great promise for a variety of applications areas, such as nanoprobe, molecular reinforcements in composites, displays, sensors, energy-storage media, and molecular electronic devices [1–3]. There have been great improvements in synthesis and purification techniques, which can now produce good-quality nanotubes in large quantities. There is a vast and enticing database from theoretical calculations and experiments that

predicts several unique opportunities for nanotube applications based on their properties. At this juncture, when one looks at the applications landscape for nanotubes and nanotube-based products, it seems appropriate to divide this landscape into three categories based on timelines: present applications that are already in the marketplace, near-term applications that will succeed in the marketplace in the next ten years, and long-term applications beyond the ten-year horizon. In the next several sections of this review we will deal with various applications where nanotubes have shown promise, within the perspective of this timeline. The summary at the end of this review (see Sect. 3) captures the big picture of carbon-nanotube applications. At the outset we would like to state that beyond these clearly visible practical uses there have been tremendous advances in the understanding of the physics and chemistry of carbon systems and this material has acted as a front runner for the whole field of nanotechnology, attracting much attention from the academic community and industry alike.

In some sense, carbon nanotubes came following the footsteps of what was a unique discovery in carbon science, the  $C_{60}$  fullerene molecule [4]. Although the fullerenes could stimulate and motivate the large scientific community, their applications remain at large to date. On the other hand, graphite and carbon fibers [5], the larger analogs of nanotubes, have been commercially used for decades. Their applications range from use as conductive fillers and mechanical structural reinforcements in composites (e.g., in the aerospace industry) to electrode materials (e.g., in batteries) (see Table 1). Although the primary bonding in graphite, carbon fibers and nanotubes is the same (the  $sp^2$ -hybridized, hexagonal honeycomb lattice); nanotubes are distinguished from the other carbon forms by their unique morphology, dimensions and defects. Carbon nanotubes approach the theoretical inplane properties of graphite, which, based on the defect-free carbon-carbon bond, provide the strongest bonding in nature. The exceptionally high modulus, electrical and thermal conductivity and elasticity of planar graphite are all reflected in the inherent properties of nanotubes, and several of the other contributions in this book have been devoted to describing these. The issues we want to discuss in this review are different; after a few decades of research and development of the nanotube material (starting from early reports by *Endo* and coworkers [6]), where do we now stand in terms of applications and what are the real commercial prospects for this material? What are the real challenges that still impede progress towards applications for nanotubes? Will the promises of the early days of nanotube reporting hold out and will nanotubes actually emerge as the leading material in the nanotechnology revolution that we foresee?

To discuss the above issues, it is imperative that we identify what we call nanotubes today with some discrimination. There are essentially two categories of nanotubes that are prevalently used today [7]. The multiwall carbon nanotubes (MWNs), which have shown the most promising appearance to the marketplace in recent times, date back to early reports of *Endo* in the late

**Table 1.** Some of the main applications of traditional graphite-based materials including carbon fibers

Traditional graphite material	Commercial applications
Graphite and graphite-based products	Materials-processing applications such as furnaces/crucibles, large electrodes in metallurgical processes, electrical and electronic devices such as electric brushes, membrane switches, variable resistors, etc., electrochemical applications for electrode materials in primary and secondary cells, separators for fuel cells, nuclear fission reactors, bearings and seals (mechanical) and dispersions such as inks. (Estimated market: 13 billions USD)
Carbon-fiber-based products	Carbon-fiber composites (Total market: ~ 1 billion USD: Aerospace (70%), sporting goods (18%), industrial equipment (7%), marine (2%), miscellaneous (3%))
Carbon-carbon composites	High-temperature structural materials, Aerospace applications such as missile nose tips, re-entry heat shields, etc., Brake-disc applications (lightweight, thermal conductivity, stability), Rotating shafts, pistons, bearings (low coefficient of friction), Biomedical implants such as bone plates (biocompatibility) (Estimated market: 202 million USD).

1970s. These were catalytically grown (by chemical vapor deposition; CVD) multilayer graphitic tubular structures that could be further annealed to decrease their defect density. The dimensions of these were typically several tens of nanometers in diameter, but occasionally smaller structures including single-layer tubular structures were also observed. In the early 1990s, *Iijima* and others [8, 9] showed that the high-temperature arc-discharge process could produce smaller, highly graphitized multiwall structures. Then came the discovery of single-wall nanotubes (SWNTs) [10, 11] in 1993 by the NEC and IBM groups that suggested that catalytic vapor deposition can be controlled to make single-layer tubular structures of graphene with diameters as small as 1 nm. The ability to grow such small defect-free graphene tubes prompted people to suggest various applications for these structures, including that of electronic devices; features such as chirality, defect-free structure and small dimensions showed possibilities of their use as quantum wires.

Carbon-based fibrillar structures at that point crossed over from the traditional graphite-like material to molecular structures with an applications domain expanding into nontraditional areas like nanoelectronics. Today, we are able to make nanotubes with a precisely tuned number of layers, such as SWNTs and double-wall nanotubes (DWNTs) and a lot of progress has occurred in the scalable synthesis of this material. It is also possible these days to synthesize in large quantities carbon nanotubes that are uniformly doped with elements such as nitrogen and these hold promise for specific applications (see the contribution by *Terrones et al.*). When the applications of nanotubes are considered, they divide between the traditional (where nanotubes provide value addition compared to carbon fibers and other carbons) and nontraditional (where nanotube applications provide unique applications) uses, often delineating the timeline expected for applications.

## 2 Applications of Carbon Nanotubes

The last couple of decades of work in fullerenes and nanotubes promised an amazing range of applications for these materials [1–3]. However, these new concepts and ideas for applications of carbon nanomaterials have had a limited success in the marketplace, mainly due to issues in processing, scaleup and more importantly due to the inability to properly assess the time frame that is needed to take new products to market, in particular if these products result in disruptive technologies. Many of the applications of fullerenes and nanotubes conform to this class, be it drug delivery using fullerenes or nanoelectronics using nanotubes. In addition, there are intrinsic challenges at the nanoscale (assembly, role of interfaces, contacts, etc.) which have also slowed the pace of progress in the applications of these new materials.

At the same time, there are a few applications of nanotubes that are indeed commercialized today. The best examples of present bulk applications of CNTs are the use of CVD-grown large multiwall nanotubes in lithium-ion batteries and in plastics for electrostatic discharge applications. Both of these applications do not utilize the spectacular mechanical or electronic properties of perfect nanotubes, but function as additives that add value to the products (mechanical stabilizing in batteries and dissipation of static electric charges in plastics). These applications cater to large volumes of nanotubes and the need has driven large-scale manufacturing of this material in the last few years. Today, the bulk volumes of manufactured MWNTs reach a few hundred tons per year. The situation of SWNTs is different with the volume of material produced per year not exceeding a few kilos. There are some indications that suggest that there could be a quantum leap in the production of SWNTs in the next few years but the drive towards this will depend on demand for this material in specific areas of applications. One potential application for SWNTs that would require large quantities of material is the field emission display, which has been widely talked about as the first major application of

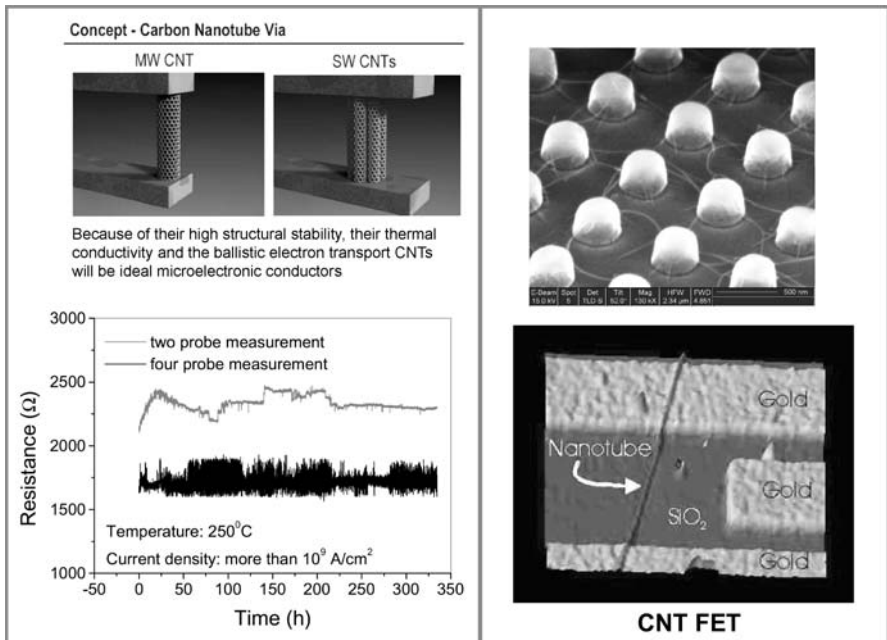
SWNTs; and prototypes have been demonstrated by large companies such as Samsung and Motorola. However, the product has not been commercialized yet, for reasons that are unknown.

This section in this chapter will deal with important application areas of both MWNTs and SWNTs. The major applications that arise from the intrinsic advantage of nanotubes will be considered in the broad areas of electronics, energy, composites, sensors, field emission, biology and other miscellaneous fields. In each of these distinct areas, the prospects of nanotubes will be described based on their known attributes, demonstrated abilities and state-of-the-art efforts that have been invested in these materials. The main theme of this chapter will be described in these subsections, pointing out whether the applications are imminent or long term. We hope that the readers gain a better understanding of carbon nanotube applications, including current challenges and potential uses in future technologies. In the final sections, some of the health and environmental effects of nanotubes will be considered. There has been a lot of scrutiny in recent times on the adverse effects of nanotubes (and nanomaterials in general) to health. Although the issue still needs systematic and long-term evaluation to properly understand the effects, it is worth pointing out what the thinking is on this issue at the present time. In the concluding section, we will make a conscious effort to list nanotube applications from two separate points of view; bulk vs. limited-volume applications and short-term versus long-term applications. These will act as a guide for readers to follow the application pathways for nanotubes in the years to come. The success of these possibilities will depend on whether some of the technical challenges described in this and other reviews elsewhere in the book can be addressed and solved within realistic time frames.

## 2.1 Carbon Nanotubes in Electronics

It should be pointed out that the integration of nanotubes into electronic devices still is a long-term application with the prospect of commercial products beyond the ten-year time frame. However, nanotubes (in particular, SWNTs) have emerged as a promising class of electronic materials due to their nanoscale dimensions and outstanding properties, such as ballistic electronic conduction [12, 13] and insensitivity to electromigration [14, 15]. Both metallic and semiconducting SWNTs are found to possess electrical characteristics that compare favorably with the best electronic materials presently available. The recent advances in the separation [16, 17] of SWNTs with different electronic properties has enabled the nanotube community to develop the field-effect transistors (FET) and interconnects on a large scale (Fig. 1).

In hot pursuit of Moore's law, semiconductor giants like Intel, IBM, AMD, UMC and TSMC are commercially manufacturing silicon-based transistors at the 65-nm technology node (Q1, 2007). Intel intends to commercialize transistors at the 45-nm technology node by the end of 2007 or early 2008 [19]. By an evolutionary process, a conservative estimate for the smallest conceivable



**Fig. 1.** *Left Panel:* Top schematic shows the possibility of using carbon nanotubes (both MWNT and SWNT bundles) as via interconnects (Courtesy of Georg Duesberg at Infineon Corporation). The problems that copper faces, such as electromigration may be overcome by using nanotubes in the vertical configuration. Bottom figure presents an experimental test showing electromigration studies of a single multiwall nanotube contacted by two probes [18]. The current-carrying capacity of nanotubes is exceptionally high. *Right Panel:* The top image shows the possibility of growing horizontal networks of single-wall nanotubes on silicon surfaces by CVD and the bottom panel shows a FET device that can be constructed from such a SWNT after properly contacting them with metal in a three-terminal configuration (bottom image, courtesy of Phaedon Avouris of the IBM Corporation)

silicon transistor at this point is 16 nm, expected to hit markets not prior to 2018. A revolutionary speedup of this process can be realistically envisioned only if nanotechnology can be controlled on a large scale. Single-wall carbon nanotubes, with a diameter of  $\sim 1$  nm, have been demonstrated to operate as field-effect transistors almost a decade ago, and since then, the FETs have steadily grown in versatility and promise for future nanometer-scale electronics.

The earliest works on room-temperature carbon-nanotube transistors were done simultaneously by the Delft [20] and the IBM groups [21]. They demonstrated that semiconducting single-wall nanotubes have a channel conductance that can be modified by orders of magnitude ( $\sim 10^5$ ) by an exter-

nally applied gate voltage, very similar to that of a MOSFET. These tube-FETs or CNT-FETs were generally p-type, and the charge transport was modulated by the modification of the Schottky barrier height at the electrical contact between the nanotube and the metal electrodes upon application of a gate voltage. Since then, a number of groups have made progressive improvements in building n-type as well as ambipolar CNT-FETs. By 2001, further important progress was made in the integration of nanotubes from simple transistors to logic circuits. One-, two-, and three-transistor circuits that exhibit a range of digital logic operations, were demonstrated such as an inverter, a logic NOR, a static random-access memory cell, and an ac ring oscillator [22]. The IBM team developed a technique to produce arrays of carbon-nanotube transistors, bypassing the need to meticulously separate metallic and semiconducting nanotubes [23]. The next half a decade saw a flurry of technological advances that demonstrated the usefulness of CNT-FETs in diverse ways. CNT power transistors were demonstrated to have 20 times less switching resistance and 200 times more current-handling capability than conventional power MOSFETs. A University of Maryland team has recently demonstrated that CNTs can have enormous carrier mobility ( $\sim 10^5$  cm<sup>2</sup>/Vs) [23]. Other researchers were able to push the feasibility of using nanotube FETs at the GHz and THz frequency range. Other innovations like using nanotube Y-junctions to form switches [24], and chemical functionalization to modify nanotube conductance have given more flexibility in design consideration for the final chip-making process.

In addition to transistors, nanotubes can also function as interconnects due to their metallic characteristics. As interconnect feature sizes shrink, copper resistivity increases due to surface and grain-boundary scatterings and also due to surface roughness [25]. In contrast, carbon nanotubes exhibit a ballistic flow of electrons with electron mean-free paths of several micrometers, and are capable of conducting very large current densities [26]. Carbon nanotubes have been shown to withstand current densities up to  $10^{10}$  A/cm<sup>2</sup>, exceeding copper by a factor of 1000. A bundle of closely packed parallel metallic carbon nanotubes, or a large defect-free MWNT are proposed to be used for the next generation of interconnects. A bundle of 400 SWNTs can be as narrow as 20 nm in diameter since making a bundle and connecting the tubes in parallel serves two main purposes. Firstly, connecting in parallel helps in overcoming the problem of the high value of the contact resistance of a single nanotube and secondly bundles ensure a lower capacitance comparable to that of a single nanotube, as opposed to the high value for a monolayer of nanotubes [27]. Moreover, with respect to resistance, nanotubes are favorable in high aspect ratio structures like vias, where also the highest current densities are expected [27]. In addition to the onchip (short as well as via) interconnects, due to the mechanical flexibility and compliance of nanotube bundles, they are also being considered for back-end (die to package, in packaging) flexible interconnects and these may be realized in a time frame faster than the integration of onchip nanotube-based structures. The intrinsic elec-

tromechanical properties of nanotubes can also be useful in the creation of probe arrays that have several uses in the microelectronics industry.

As indicated before, many groups have now successfully made FETs with semiconducting carbon nanotubes as the channel in their transistors [28, 29]. Semiconducting carbon-nanotube FETs have successfully shown an ON to OFF ratio of conductance,  $G_{\text{ON}}/G_{\text{OFF}} \sim 10^5$  [30]. Moreover, thin films of high-dielectric materials, such as  $\text{ZrO}_2$  and  $\text{HfO}_2$  ( $\kappa \sim 15\text{--}25$ ), are highly desirable for gate dielectric integration in field-effect transistors as they enable high ON-state current densities (speed) and low operating power consumptions. The integration of high- $\kappa$  dielectrics, however, has been a challenge in planar MOSFETs because of the inherent mobility degradation of the Si channels. A unique advantage of carbon nanotubes is their compatibility with high- $\kappa$  dielectrics. The lack of dangling bonds at the nanotube/high- $\kappa$  interface and the weak noncovalent bonding interactions between the two materials prevent any perturbation to the electron transport in nanotubes.

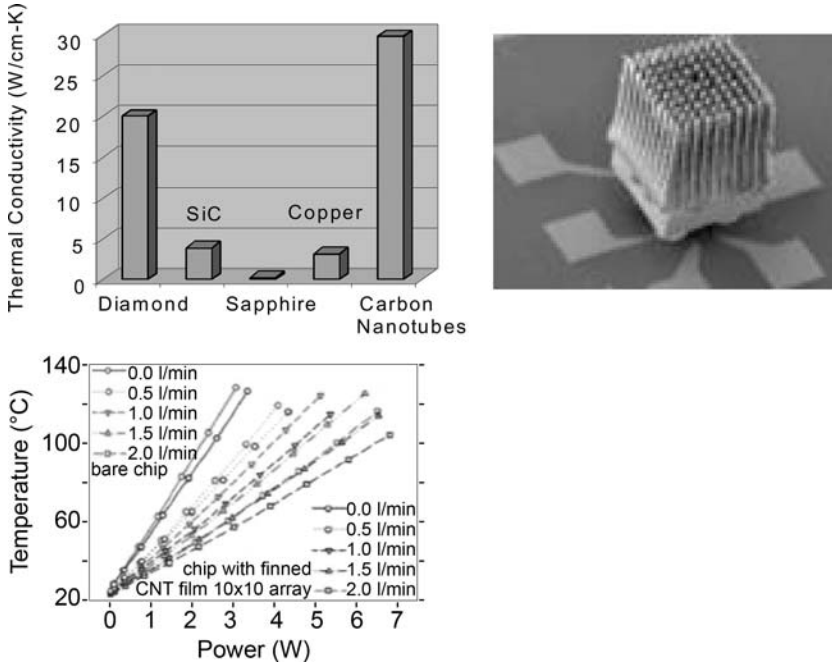
Another important achievement is the development of an electromechanical memory device by Nanterro Inc., a startup company focused on bringing on the first major electronic application of nanotubes. Owing to their mechanical resilience and electrical conductivity, CNTs (carbon nanotubes) can perform as sensitive nanoelectromechanical devices such as nonvolatile memory. Using a crossbar layered architecture, Nanterro is developing a bistable memory device that can be actuated electrostatically [31]. Since direct growth of such structures is challenging, the structure is made from thin membranes that are suspended above prefabricated electrodes and it seems that these devices can be operated at low voltages for millions of cycles at high switching speed. This device, which is being codeveloped by LSI Logic, is poised to enter the market in the next few years.

Invisible circuits based on transparent transistors have found broad potential applications in consumer, military, and industrial electronic systems. The quest for flexible and transparent transistors made from SWNTs has resulted in several noteworthy achievements [31]. SWNTs have recently been used to make all of the conducting (i.e., source, drain, and gate electrodes) and semiconducting layers, respectively, of a transparent, mechanically flexible, thin-film transistor (TFT) [32]. These devices are fabricated on plastic substrates using layer-by-layer transfer printing of SWNT networks grown using optimized chemical vapor deposition (CVD) procedures. The unique properties of the SWNT networks lead to electrical (good performance on plastic), optical (transparent at visible wavelengths), and mechanical (extremely bendable) characteristics in these TFTs that would be difficult, or impossible, to achieve with conventional materials. Similar work [33] has shown integration of transparent SWNT electrodes with organic semiconductors to form flexible TTFTs (transparent thin-film transistors) on plastic substrates. These devices have shown good electrical properties including negligible contact resistances, mobilities larger than  $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , mechanical flexibility (radii of curvature  $< 5 \text{ mm}$ ) and optical transparency (70%). In addition,

there have also been successful attempts at manufacturing ultrathin, transparent, optically homogeneous, electrically conducting films of pure SWNTs and DWNTs and transferring those films to various substrates [34]. These films exhibit conductivity and transparency performances equivalent to the commercially used transparent conductor indium tin oxide (ITO) but have better transparency in the important infrared bandwidth range. One day, the transparent nanotube films could replace ITO, at least in applications such as displays and touch screens and even LEDs at a later stage. The challenge here is to get relatively high transparency ( $> 90\%$ ) simultaneously with high conductance.

Some of the existing and near-term electrical applications of nanotubes are in areas where the high aspect ratio, and high electrical conductivity of nanotubes with good dispersion (at a few wt% loadings) in polymer matrices enables excellent electrical percolation leading to electrostatic discharge (ESD) and electrical-shielding applications [35]. For ESD applications, the nanotubes prevent charge buildup on the surface of the insulating plastic. Today, large (tonnage) quantities of multiwall nanotubes and nanofibrils are manufactured by the company Hyperion Catalysis International and supplied as premixed material in thermoplastics to the General Electric (GE) company for use in their engineering plastics that are employed in automobile body parts. This remains as one of the biggest bulk application of nanotubes today. The first commercial applications for MWNTs make use of their properties to address electrostatic discharge. The applications also include high-end microelectronics products where static electric discharge from packaging components can destroy electronic chip components. In addition to the ESD application, electromagnetic interference (EMI) shielding applications have also been pursued [5] for nanotubes at high loadings, utilizing the extremely high conductivity of nanotubes. Carbon fibers have been used in this area and unless nanotubes offer significant advantages compared to the traditional fillers, it is not clear if nanotube-based plastics would outperform conventional materials in EMI shielding.

Another area where nanotubes could bring in change (in the 5–10 year time frame) is in the area of onchip thermal management. High power consumption and the corresponding problem of heat dissipation is one of the biggest issues in high-performance microprocessors today. There have been several reports pointing out the record axial thermal conductivity of individual nanotubes. It has been recently shown by several groups that efficient cooling can be achieved on silicon chips using aligned carbon nanotube arrays (MWNTs) [36]. Tiny cooling elements can be fabricated and mounted on chips to enable significantly enhanced power dissipation from the heated chips and hot spots (Fig. 2). The cooling performance observed for nanotube structures makes them viable candidates for onchip thermal management. The issue here is that of thermal interfaces where scattering leads to dissipation of thermal energy. For efficient application, the thermal contact resistance needs to be decreased. The high thermal anisotropy of nanotube

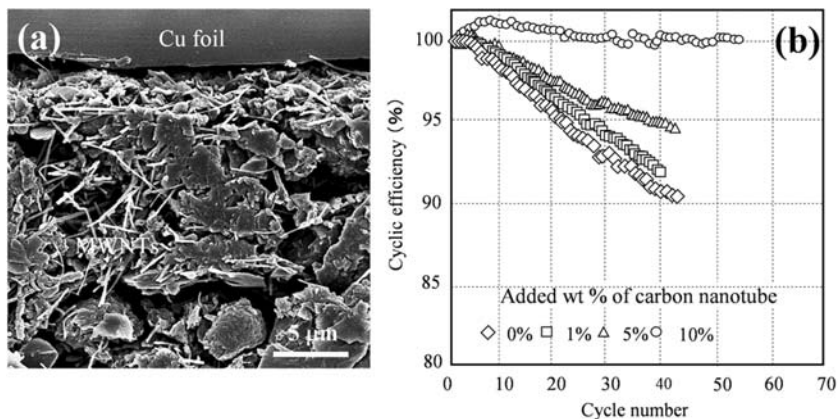


**Fig. 2.** *Clockwise from top left:* Plot shows the comparison of the thermal conductivity of nanotubes with the best (thermally conducting) materials. The high thermal conductivity along the tube axis (conductivity is highly anisotropic due to the structure) allows the material to be used in thermal management, for example, onchip cooling. The SEM image shows a fin structure constructed from a uniformly aligned array of MWNTs using laser machining. The fin structure is flipchip bonded to a silicon substrate on a thermocouple device that has been printed for temperature measurements. *Graph in the bottom panel* shows chip temperatures measured for chip-on-substrate and for the corresponding MWNT  $10 \times 10$  fin array-on-chip-on-substrate assemblies under various heating powers and N<sub>2</sub> flow rates. It was seen that with the MWNT fin attachment, the cooling efficiency under forced flow improved by about 20% [36]

structures (high axial conductivity versus poor transverse conductivity) can be a challenge or an advantage when designing cooling architectures based on aligned nanotube structures.

## 2.2 Carbon Nanotubes in Energy Applications

Conventional carbon materials have been utilized either as the electrode materials themselves or the conductive filler for the active materials in various electrochemical energy-storage systems due to their good chemical stability and high electrical conductivity. Therefore, it is natural that carbon nanotubes have been adopted as the preferred alternative electrode mate-



**Fig. 3.** (a) FE-SEM micrographs of the anode sheet containing carbon nanofibers/nanotubes in a commercial Li-ion battery, and (b) the cyclic efficiency of synthetic graphite, heat treated at  $2800^{\circ}\text{C}$ , for samples with various weight per cent nanotubes, in the range 0 to 1.5 V, with a current density of  $0.2\text{ mA/cm}^2$  [44]

rial because they have unique electrical and electronic properties, a wide electrochemical-stability window, and a highly accessible surface area. With regard to energy generation and storage, nanotubes show great promise in supercapacitors, Li-ion batteries, solar cells and fuel cells; and energy applications could become the largest applications domain in the bulk application of nanotubes. At the same time, one major energy application that initially generated a lot of interest for nanotubes, namely hydrogen-storage, is now considered as not viable because careful studies have shown that the hydrogen-storage capacity of nanotubes at room temperature is far too low to generate any practical interest.

The high potential of carbon nanotubes as the electrodes in lithium-ion batteries (LIBs) has been suggested [37–40] because carbon nanotubes exhibited an increased reversible capacity up to  $1000\text{ mA h/g}$  [41]. Unfortunately, the large reversible capacity, the absence of a voltage plateau, and the large hysteresis, that are observed in a typical hard carbon [42], limited the use of nanotubes as the electrode material in LIBs. On the other hand, carbon nanotubes have been commercialized as the filler of choice for the anode materials used in LIBs [43]. Homogeneously dispersed carbon nanotubes in synthetic graphite (ca. 3 wt %) give rise to a continuous conductive network as well as a mechanically strong electrode, resulting in a doubled energy efficiency of LIBs (see Fig. 3) [44]. Nitrogen-doped CNTs and nanofibers have also shown efficient reversible energy storage in LIBs ( $480\text{ mA h/g}$ ), higher compared to commercial carbon materials used for LIBs ( $330\text{ mA h/g}$ ).

For energy-storage devices other than batteries, supercapacitors have been extensively and actively investigated because they are able to store and deliver energy rapidly and efficiently for a long life cycle via a simple charge-

separation process [45]. In addition, their wide range of power capability makes it possible to hybridize them with other energy-storage devices, such as batteries and fuel cells. Even though they are being used now in various types of electronic devices (e.g., memory backup), from computers to vehicles, their intrinsic low energy density has blocked the maturation of their market. In this context, supercapacitors with carbon-nanotube electrodes have been evaluated to increase their energy density [46, 47]. For example, a SWNT electrode exhibited the maximum reported capacitance of ca. 180 F/g and a power density in the range of 6.5–7 Wh/kg [47]. Also, chemically modified MWNTs are in the early stage of commercialization for use as a conductive filler for porous carbon materials for high-power supercapacitors [48].

Silicon-based photovoltaics have reached solar-energy conversion efficiencies of  $\sim 25\%$ ; however, this technology requires environmentally hazardous processing and has proven to be too expensive to replace nonrenewable energy sources for widespread application. A different option is to use organic thin films of conjugated polymers, which, although having relatively low conversion efficiencies ( $\sim 5\%$ ), would be lower in cost compared to silicon-based technologies. Conjugated polymers are able to absorb a photon and generate an exciton that can dissociate into an electron–hole pair under the strong electric field found at polymer/metal interfaces. The most efficient design for organic solar cells uses a bulk heterojunction composite of a conjugated polymer with nanoscale electron acceptors forming a percolating network through the thin film. This maximizes the interfacial area between the metal filler material and the polymer, which promotes charge separation and allows conduction of the electrons through the percolating network to be collected at the electrode. For an organic solar cell to be commercially viable and to compete with silicon-based technologies it will need to reach an energy conversion efficiency of 5–10%, have a lifetime of at least 5 years and cost less than 1/peak watt.

Carbon nanotubes can be a good material for forming bulk heterojunctions in organic solar cells (Fig. 4). Their high aspect ratio allows formation of a percolating network of nanotubes at low doping levels in a polymer composite [49, 50]. As one-dimensional nanostructures, nanotubes are also ideal for electron transport as they exhibit quasiballistic features [51, 52]. The general device design for a bulk heterojunction organic solar cells is a sandwich structure (Fig. 4) consisting of a transparent conducting electrode, typically indium tin oxide (ITO) or fluoride tin oxide (FTO), coated on a glass or PET substrate, a layer of Poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS), a layer of the composite material, and a thermally evaporated electrode on the top of the composite layer, typically aluminum. Ultrasonication is used to disperse nanotubes in the conjugated polymer, followed by centrifugation to remove large aggregates. The composite solution is then deposited on the transparent electrode either by drop casting or spin casting.



**Fig. 4.** Sandwich structure of bulk heterojunction organic thin-film photovoltaic cell. Glass or PET substrate is first coated with ITO or FTO, which is transparent and conductive. PEDOT:PSS is spin coated on top of the ITO to promote hole mobility into the electrode. The bulk heterojunction nanotube composite is then layered onto the device and an aluminum electrode is thermally evaporated on top of the nanotube composite [50, 51, 53–57]

*Kymakis* and coworkers [53, 54] first demonstrated in 2002 that SWNTs dispersed in poly(3-octylthiophene) (P3OT) showed an increase in short-circuit current,  $I_{SC}$ , by 2 orders of magnitude compared to P3OT alone in an ITO/composite/aluminum sandwiched device. As the light intensity increases the device also yields larger photocurrents, as expected from an increase in the formation of excitons in the composite materials. In 2005 they were able to improve the device performance by coating the ITO electrode with PEDOT:PSS that helps to promote hole injection into the ITO [55]. This device had an increase in power conversion efficiency from  $2.5 \times 10^{-5}$  to 0.1% compared to P3OT alone. By varying the percentage of SWNTs in the composite the maximum efficiency was found at 1% SWNTs, as higher loading limited the photocurrent due to a lower photogeneration rate from the polymer.

Carbon nanotubes have also been utilized in different conjugated polymer matrices with improvement in charge separation and transport. Various research groups have achieved a 2–6 fold increase in the photoresponse of the composite compared to the pure polymer [51, 58–65]. Devices of composites with water-soluble conducting polymers have the potential to lead to more environmentally benign processing and reduced production costs [59, 64]. The efficiencies of these devices are not high enough to be of much commercial interest at this point, but this enhancement is promising for long-term development.

Bulk heterojunctions of nanotubes in organic conjugated polymers have led to improved exciton dissociation and charge transport; however, these devices are not optimized to absorb light over the entire solar spectrum. The solar spectrum has a maximum in light intensity between 500–800 nm, but many semiconducting polymers do not absorb strongly in this region. One approach to improving the absorption of light in this region is to incorporate organic dyes with high absorption coefficients at the nanotube/polymer interface that absorb strongly in the peak intensity region of the solar spectra [66, 67]. Several groups have demonstrated an improvement in SWNT- or MWNT-based solar cells with this approach. *Bhattacharyya* et al. [56] reported the enhancement in device performance by incorporating a dye with aromatic

pyrenyl groups N-(1-pyrenyl)maleimide (PM) into a SWNT/P3OT device. Naphthalocyanine (NaPc) was used by *Kymakis* and *Amaratunga* [57] as the sensitizer in a SWNT/P3OT device. For this particular device there was an enhancement by a factor of 20 of the photocurrent with the dye compared to the dark. Naphthalocyanine has also been used in MWNT-poly(3-hexylthiophene) composites to drastically improve the absorption in the visible region, promoting a higher generation rate of excitons.

Nanotube-based hybrids can also be designed to aid exciton generation and charge separation using quantum dots and nanoparticles. In 2005, quantum dot-SWNT hybrid devices were designed by the *Landi* group to take advantage of the QD (quantum dot) electron affinity and the low doping levels of SWNTs [49]. Photovoltaic performance from this composite demonstrated a  $V_{OC}$  similar to the previous SWNT/P3OT but had a limited efficiency, which was attributed to interfacial defects at the device junctions. Titania nanoparticles can also be used to enhance the device performance using electrostatic linking. *Feng* et al. [68] used acid-functionalized MWNTs to attach  $TiO_2$  nanoparticles and observed a twofold photocurrent increase over a device without nanotubes.

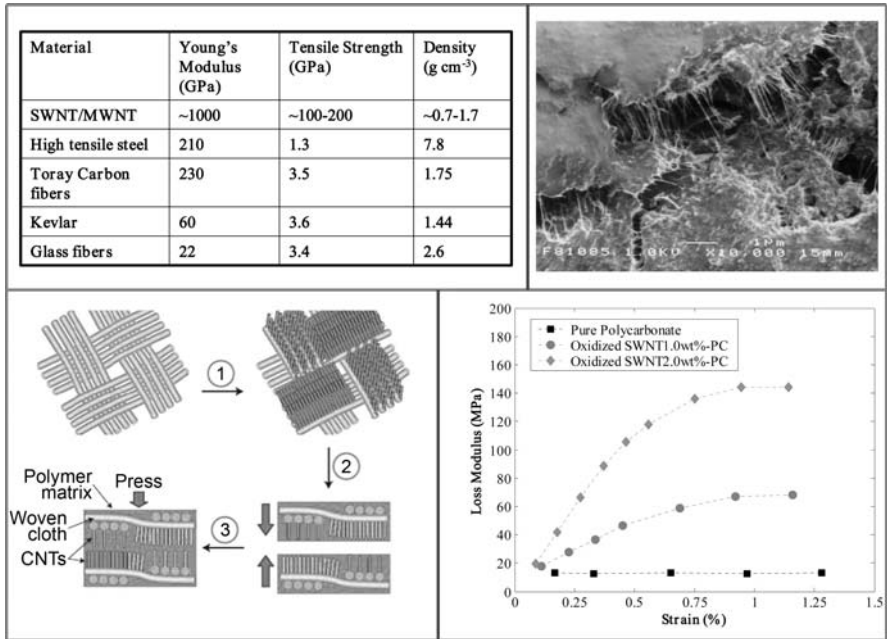
Semiconducting carbon nanotubes can generate excitons upon absorption of near-infrared light, which can increase overall exciton generation in the device as well as expand the range of light that can be absorbed simultaneously [69, 70]. The science of excitons in carbon nanotubes is discussed in the contributions by *Spataru* et al. [69], *Ando* and *Kono* et al. *Kazaoui* et al. [71] has demonstrated, using a SWNT/poly[2-methoxy, 5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEHPPV) or SWNT/P3OT composite with Al and ITO electrodes in a sandwich structure, that the range of photoresponse can be extended past the visible to a range of 300–1600 nm. The photocurrent response from the devices in a range from 900–1500 nm matches the optical absorbance features of semiconducting SWNTs. Below 900 nm the photocurrent is dominated by exciton generation from MEHPPV or P3OT. The science of carbon nanotubes optoelectronics is discussed in detail in the contribution by *Avouris* et al.

Carbon nanotubes have proven to be promising materials for bulk heterojunctions in organic thin-film solar cells. These devices have shown improvement in charge separation and transport but currently perform at relatively low efficiencies. Even with these efficiencies there is interest to move forward with commercialization for low-power applications in the next few years. With further enhancement and optimization of the nanotube/polymer interface these materials are expected to be able to reach energy-conversion efficiencies of 15–20% in the next ten years. The focus in present development must be to improve device efficiency as well as the lifetime of the cell in order to be a competitive technology with silicon cells. At this point the most promising routes forward are in dye sensitization and nanoparticle hybrids to improve exciton generation and charge separation.

In the field of fuel-cell systems, carbon nanotubes are very promising as supporting materials for Pt catalyst [72, 73]. Experimentally, stacked-cup carbon nanotubes [74] and nanohorns [75] with a large portion of reactive edge sites were effective to anchor homogeneously distributed small-sized Pt catalysts, and this resulted in a doubled fuel-cell performance [76]. The National Institute of Standards and Technology (NIST) in collaboration with Carbon Nanotechnologies, Inc., Motorola, Inc. and Johnson Matthey Fuel Cells, Inc. is planning to develop “free-standing” carbon-nanotube electrodes for micro-fuel cells in order to meet the ever-growing demand for more power and longer run times in portable microelectronics. In particular, higher efficiency for proton-exchange membrane fuel cells (PEMFC) have been demonstrated using Pt catalysts supported on MWNTs [77]. This application looks very promising and could find a marketplace in less than 5 years.

### 2.3 Carbon Nanotubes for Mechanical Applications

The mechanical and structural applications of carbon nanotubes also hold potential to be the biggest large-scale application for the material. The mechanical, and thermal properties of carbon nanotubes are discussed in detail in the contribution by *Yamamoto* et al. Nanotubes are considered to be the ideal form of fibers with superior mechanical properties compared to the best carbon fibers, the latter of which already has fifty times the specific strength (strength/density) of steel and are excellent load-bearing reinforcements in composites [1]. Carbon fibers have been used as reinforcements in high strength, light weight, high-performance composites; one can typically find these in a range of products ranging from expensive tennis rackets to spacecraft and aircraft body parts (see Table 1). Ideally, nanotubes should perform far better than these fibers in mechanical applications. The observed tensile strength of individual nanotubes could come close to a few 100 GPa and their elastic modulus in the terapascal range [78–80], far better than traditional carbon fibers. Nanotubes can sustain large strains under compression. The reversibility of deformations, such as buckling, has been studied [81]. Flexibility and compliance of nanotubes depends on the geometric parameters of the nanotubes, which can be tailored. Such flexibility of nanotubes under mechanical loading is important for their potential application as nanoprobe and in electromechanical applications [82]. The near-ideal properties of nanotubes have prompted several groups, the most prominent among them being NASA, to invest large amounts of resources in developing carbon-nanotube-based composites for applications in aerospace (Fig. 5). Although nanotubes have near perfect structures and high aspect ratios, there are stiff challenges in adapting these materials for structural applications. Needless to say, there has not been significant progress, even after a decade of research, in developing nanotube (as load-bearing filler material)-based composites that outperform the best carbon-fiber composites.



**Fig. 5.** *Top panel:* Left table shows a comparison of the mechanical properties of nanotubes compared with other structural materials, making them attractive for composite applications. Right figure is an SEM image showing the fracture surface of an epoxy-SWNT composite, exposing the stretched nanotubes in the crack [83]. Processing of nanotube composites is a challenging task due to poor dispersions obtained in most cases. *Bottom panel:* Left schematic (from [84]) shows the possibility of taking traditional stacked fiber panel composites and adding an interfacial layer of nanotubes that bridges the panels that hold the oriented fibers (SiC or carbon fiber, for example). The interfacial nanotube layer acts like a velcro, stiffening the adjacent stacks and helping to improve the through-thickness properties of 3D composites. Right plot shows loss modulus of SWNT-polycarbonate composites, showing the excellent improvement in vibrational damping properties (measured by the loss modulus) with the addition of nanotubes [85]

Although nanotube-filled polymer composites could have obvious advantages, the main problem seems to be in creating a good interface between nanotubes and the polymer matrix and attaining good load transfer from the matrix to the nanotubes during loading [83, 86]. The reason for this is that nanotubes are atomically smooth and unless properly engineered, the interface between nanotubes and the polymer matrix remains weak. Secondly, nanotubes are almost always organized into aggregates (concentric arrangement within MWNTs and as bundles in SWNTs) that behave differently in response to a load, as compared to individual nanotubes. Earlier studies of load transfer using Raman spectroscopy suggested that simply mixing

nanotubes into a polymer does not guarantee good load transfer [86]. Hence, recent approaches have all been based on chemically modifying the surface functionalities of nanotubes so that strong interfaces can be created [87]. In addition to these intrinsic problems, processing of nanotube-filled polymers (e.g., epoxy) remains difficult since even a low wt% of the nanotubes (< 5%) increases viscosity prohibitively, making processing difficult. Finally, one needs to appreciate the fact that even with the very high aspect ratios, nanotubes essentially belong to the category of short fibers, which are not ideal structural reinforcements compared to continuous fiber reinforcements in composites. The role of nanotubes in composites may turn out to be a different one compared to what had been initially envisioned; more than as active load-bearing fibers in the composites, nanotubes could play the role of matrix additives, providing multifunctional properties to the composite. Even with these challenges, there are several companies in the USA (e.g., Zyvex corporation) and Japan (e.g., Mistui Corporation, Toray) who are developing nanotube-blended plastics for making superior sporting goods and some of the products promising better performance are already in the market. These utilize the CVD-grown MWNTs and nanofibrils as their nanotube additive. Once again, nanotubes in these products act more as matrix enhancers rather than as the primary load-bearing structures.

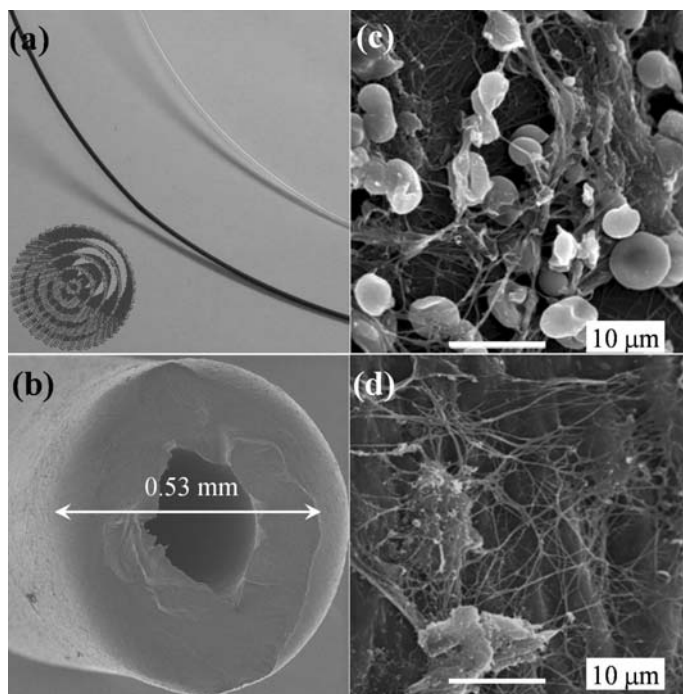
In a very different approach, it has been shown recently that nanotubes can improve properties of 3D composite [84] (Fig. 5). Here again, nanotubes are not the main load-bearing fibers, but add value to the composite in the direction normal to the plane of the fibers. Traditional fiber-reinforced composite materials made of oriented fiber stacks embedded in a polymer have excellent inplane properties but fare poorly in through-thickness (normal to the stacks and fiber direction) properties. There have been several approaches, particularly via new fiber-packing designs, but all these have had only limited success. Aligned interlaminar carbon-nanotube arrays (CVD grown directly onto SiC fiber stacks) provide enhanced multifunctional properties along the thickness direction. The carbon-nanotube arrays allow the fastening of adjacent plies in the 3D composite, providing the much-needed interlaminar strength and toughness under various loading conditions. For the fabricated 3D composites in which nanotubes are incorporated, remarkable improvements in the interlaminar fracture toughness, delamination resistance, through-thickness mechanical properties and damping, were observed. Furthermore, the inplane properties of the composites were not compromised at the same time. Such value-added propositions using nanotubes incorporated in unique geometries to traditional composites are welcome applications of nanotubes in the area of structural polymer composites.

The interfacial weakness when one adds nanotubes to polymer matrices can be converted to a strength in terms of application in the area of vibration damping. Damping alleviation is a major issue in aerospace as well as automobile applications, and the successful implementation of nanotubes for vibration damping has been recently demonstrated [85, 88, 89] (Fig. 5). Work

has shown that the nanotube-matrix sliding energy-dissipation mechanism can induce a nearly three orders of magnitude increase in loss modulus of a polymer matrix with a relatively small (1–2%) weight fraction of well-dispersed SWNT fillers. Impressive damping increases in epoxy as well as other high-temperature resins have been shown using SWNT fillers. If large-scale manufacturing of nanotube-based composites can be implemented in a scalable way, nanotube fillers as damping elements in composites could become a real bulk application. These applications of nanotubes in composites are still in the developmental stage and although the composite application of nanotubes was taken for granted, it will take several more years to evaluate the effectiveness of nanotube composite systems versus traditionally fiber-reinforced composites. In the best scenario, nanotubes in composites would provide multifunctionality (matrix stiffness, damping, conductivity, ESD, etc.) rather than simply acting as mechanical reinforcements.

Given that pristine nanotubes provide poor interfaces between polymers, there have been attempts to use doped nanotube structures for better interfacial strength, which is crucial in composites. Preliminary studies on the preparation of epoxy composites using N-doped MWNTs revealed a substantial increase in the glass-transition temperature with incorporation of small amounts (2.5 wt %) of nitrogen-doped MWNTs. More recently, it has been demonstrated that it is possible to grow polystyrene (PS) on the surface of N-doped MWNTs [90] and nitroxide-mediated radical polymerization [91] without using any acid treatment that is now typically done on carbon tubes to create defects. This demonstrates that inplane doping is important in the establishment of covalent bonds between the nanotube surfaces and polymer chains. Recent mechanical and electrical tests have demonstrated that PS-grafted doped nanotubes exhibit enhanced properties when compared to mixtures of PS and pristine doped nanotubes. These studies are motivating further work in the fabrication of strong, conducting composites. Terrones et al. and *Kavan* et al. discuss the chemical and electro-chemical doping of carbon nanotubes in their respective contributions.

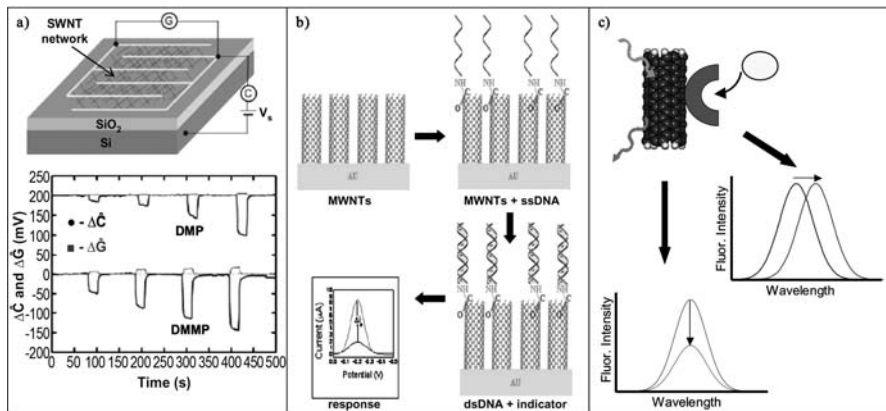
The potential uses of nanotube-filled polymers in the medical field, such as the microcatheter, have been explored [92]. Homogeneously dispersed carbon nanotubes in nylon polymer enable microcatheters to have small-sized (0.53 mm) outer diameters, two times greater mechanical strength, black color, and highly reduced thrombogenicity and blood coagulability, as compared with a pure polymer microcatheter (Fig. 6). In addition, stable biological responses of nanotube-filled microcatheters were confirmed by measuring the systematic T-cells and a histopathological study [93]. Thus, it is clear that the carbon-nanotube-filled composite-derived catheter exhibited outstanding properties when compared with a neat polymer-derived catheter, and it is envisaged that these systems will be widely utilized in various medical devices.



**Fig. 6.** (a) SEM photographs of transparent nylon-derived and opaque black nanotube-filled nanocomposite-derived microcatheters, (b) cross section of microcatheter with a hollow core, SEM images of the extraluminal surface for (c) control and (d) nanotube-filled microcatheters, respectively (taken from [92,93])

## 2.4 Carbon-Nanotube Sensors

Carbon nanotubes have been effective as sensing elements utilizing their electrical, electrochemical and optical properties (Fig. 7). Detecting a low concentration of toxic gases is important for environmental purposes and chemical safety. SWNTs have been highlighted as promising gas-sensing elements due to the 1-dimensional electronic structure with all the atoms residing only on the surface. SWNTs have advantages over conventional metal-oxide-based sensors in terms of power consumption, sensitivity, miniaturization, and reliable mass production [94]. In 2000 *Kong et al.* [95] reported a conductance change of up to three orders of magnitude from individual semiconducting SWNTs within several seconds of exposure to  $\text{NH}_3$  and  $\text{NO}_2$  gas. This prototype SWNT gas sensor, including most up-to-date follow-ups, had an arrangement based on a field-effect transistor (FET). The conductance change of a back-gated SWNT channel upon analyte adsorption is monitored via source/drain electrodes. The untreated SWNT-FET typically shows a p-type behavior, with threshold voltages being shifted upon gas exposure.



**Fig. 7.** (a) Gas sensors: Most SWNT gas sensors have an electrically contacted nanotube network on a  $\text{SiO}_2$  layer, where the array conductance ( $G$ ) is monitored upon exposure to the gas-phase analyte. It can be backgated for characterization or modification of the sensor. *Snow* et al. recently demonstrated that the capacitance ( $C$ ) between the SWNT network and Si substrate can be monitored simultaneously. Normalized capacitance and conductance responses to dimethyl phosphite (DMP) and dimethyl methylphosphonate (DMMP) are shown [34]; (b) Electrochemical sensors: There is a wide variety of electrochemical sensors utilizing CNTs. In the DNA-hybridization sensor shown, DNA is covalently attached to MWNTs on a gold substrate. After hybridization, either methylene blue or daunomycin can be used to induce a current change [42]; (c) Optical sensors: The near-infrared fluorescence of noncovalently functionalized SWNTs is exploited for biological detection. Binding of the analyte to the immobilized target results in a SWNT surface event that modulates the SWNT fluorescence. In the glucose-detection system, the fluorescence intensity is modulated [96]. In the DNA hybridization and metal-cation detection systems, the energy of the fluorescence maxima gets shifted in wavelength [97, 98]

Electron charge transfer between a SWNT and an adsorbed analyte was shown to occur both theoretically [99] and experimentally [100]. However, it has been unclear as to how the signal transduction occurs in a SWNT-FET. A general thought is that exposure to electron-donating gases such as  $\text{NH}_3$  shifts the Fermi level away from the valence band, causing hole depletion and conductance decrease. For electron-withdrawing gases (i.e.,  $\text{NO}_2$ ), conversely, the Fermi level shifting closer to the valence band creates more hole carriers and increases the conductance. Since *Heinze* et al. [101] showed that a SWNT-FET operates as an unconventional Schottky barrier transistor, several studies have been reported on the role of the SWNT–metal contact. *Bradley* and coworkers [102] first showed experimentally that the signal was not from the contact, by exposing contact-passivated sensors to  $\text{NH}_3$  and polyethyleneimine (PEI). Similar results were obtained for thionyl

chloride [100] However, a recent study by *Zhang* et al. [103] verified that  $\text{NO}_2$  sensing occurs primarily at the interface between the nanotube and electrodes. Thorough studies on various analytes are required to clarify the sensing mechanism.

Most effort so far has been on improving the sensitivity and selectivity. A common approach is to functionalize the nanotube surface with selectively binding ligands such as polymers.  $\text{NO}_2$  at the parts-per-trillion level was detected selectively over  $\text{NH}_3$  from a PEI-functionalized SWNT array, whereas selectivity for  $\text{NH}_3$  was achieved by nafion-functionalization [94]. SWNT arrays become n-type upon functionalization with electron-rich PEI, and this provides higher binding affinity for the electron-withdrawing  $\text{NO}_2$ . The array was decorated with transition-metal nanoparticles for the analytes with little electron donor or acceptor properties (i.e.,  $\text{CH}_4$ , CO) [104]. It is proposed that the formation of a transition metal-analyte complex facilitates the charge transfer between the nanotube and metal nanoparticle. *Staii* et al. [105] recently utilized DNA-decorated SWNTs for various analytes with the sensitivity being tuned by varying the DNA sequences.

Robustness of the sensor is a critical factor for long-term applications. It is noticed for many analytes that the sensor signal is not restored to its initial value, which is caused by irreversible analyte adsorption on the nanotube surface. Hence, the array has to be regenerated from these analytes. *Kong* et al. [95] were able to thermally desorb the analyte. A molecular photodesorption via UV irradiation [106] as well as a gate bias [107] were shown to effectively regenerate the surface. Hydrolysis can be a facile method for moisture-sensitive analytes [100].

In 2005 *Snow* et al. [108] demonstrated a novel SWNT chemicapacitor for gas sensing. An optically transparent but electrically continuous SWNT network was grown on thermal silicon oxide by CVD, and interdigitated electrodes were patterned on the SWNT layer. Analytes are polarized by an electric field from the SWNT network, causing an increase in capacitance. This chemicapacitor is highly sensitive, fast, and completely reversible. Functionalization with chemoselective polymers enabled ppb-level detection of dimethyl methylphosphonate (DMMP), a simulant for the nerve agent sarin. Another advantage of this configuration is that the capacitance and conductance can be monitored simultaneously. The follow-up study revealed the ratio of the conductance to capacitance response to be analyte specific and concentration independent [109]. This result suggests an unknown gas can be identified by this ratio.

Commercial carbon-nanotube gas sensors are already on the market. One sensor, from Nanomix, is for industrial-level hydrogen detection where nanotube networks were grown on a silicon substrate and electrically contacted. A top recognition layer designed for selective hydrogen binding was then applied to the array. A significant improvement in cross-sensitivity, compared to other commercialized products based upon catalytic beads or metal oxides, has been demonstrated with common interferants such as CO,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,

$\text{NH}_3$ , and  $\text{CH}_4$ . Tuning the recognition layer enabled a  $\text{CO}_2$ -detection device for breath analysis as well. Synthesis of robust selective binding ligands, in conjunction with a recent achievement in nanotube separation by electronic structure, is critical for further development in this area.

Carbon nanotubes are excellent materials for use as electrodes in electrochemical sensors due to fast electron-transfer kinetics from a number of electroactive species. A wide range of sensor architectures have been developed ranging from carbon-nanotube paste electrodes (CNTPE), glassy carbon electrodes (GCE) modified by CNTs, metal nanoparticle-modified CNT electrodes, to CNTs embedded in a conducting polymer matrix. Many sensing methodologies involve immobilizing enzymes at the CNT electrode, either through electrostatic forces or through covalent attachment. Glucose sensing has been a major thrust of electrochemical biosensor development. The majority of electrochemical glucose sensors utilize the enzyme glucose oxidase (GOx), which catalyzes the oxidation of  $\beta$ -D-glucose to D-glucono-1,5-lactone with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as a reaction byproduct. The generated  $\text{H}_2\text{O}_2$  is then oxidized at the electrode and detected by measuring current flow. The first sensor to use such a configuration was made by *Sotiropoulou* and *Chaniotakis* [36] using multiwall carbon nanotubes (MWNTs) grown directly on a Pt electrode. The device was fabricated by adsorbing GOx to carboxylic acid groups functionalized to the MWNTs. *Wang* and *Musameh* [110] encapsulated MWNTs in a Teflon matrix along with GOx on a GCE, and demonstrated a marked increase in sensitivity of glucose detection compared to an analogous device made with graphite. Similarly, *Gao* et al. [111] embedded MWNTs and GOx in a conducting matrix of polypyrrole and showed a roughly linear response to glucose in the range of 0–20 mM. *Tang* et al. employed a different sensing architecture by incorporating Pt nanoparticles in a Nafion/GOx/MWNT electrode [112]. The use of Pt nanoparticles was extended to SWNT by *Hrapovic* et al. for Nafion/GOx/SWNT on a GCE and demonstrated a sensitivity of 0.5  $\mu\text{M}$  [113]. The sensitivity of the device was further increased through the use of Cu nanoparticles to 250  $\mu\text{M}$  [114]. The major drawback to such devices is that the linear response range usually does not cover a large enough range of glucose concentrations.

In addition to glucose, a large number of devices have been made for the electrochemical detection of DNA. Single-stranded DNA (ssDNA) is immobilized on the electrode and current changes are monitored upon DNA hybridization with a complementary strand. Usually, a redox indicator that has higher affinity for double-stranded DNA (dsDNA) is used to change the electrochemical response. The first such sensor was fabricated by *Cai* et al. [115] using a MWNT/GCE and the intercalating agent daunomycin (Dmc). Methylene blue has also been used as a redox indicator for DNA detection [116]. Methods for reagentless DNA detection by monitoring oxidation of guanine have also been developed [117, 118]. A number of other analytes have been detected using electrochemical means. The first instance of using carbon nanotubes as electrochemical sensors was by *Ajayan* and coworkers [119],

who observed reversible oxidation of dopamine at a multiwall carbon nanotube electrode. A number of groups have reported direct electron transfer to nanotube electrodes from redox enzymes such as GOx [120, 121] and Cytochrome c. [122] Other detected analytes include NAD<sup>+</sup> [123], cholesterol [124] and indole acetic acid [125]. Because electrochemical sensors utilizing nanotubes are the most mature CNT-based biosensing technology, commercialization is expected to happen sooner than for any of the biosensors discussed below. However, utilization of CNTs in commercial biosensors faces a number of hurdles and as such are not expected to be available in the near term.

Semiconducting SWNTs have been fabricated into field-effect transistor (FET) devices. Such devices have been found to be very sensitive to adsorption events on the nanotube surface [95]. The first SWNT-FET for biosensing was developed by *Besteman* et al. [126] by attaching GOx, via a linker, to single SWNTs, demonstrating a slight conductance change upon addition of glucose. *Chen* et al. [127] demonstrated specific protein detection by first functionalizing the nanotubes with a target ligand, either biotin, staphylococcal protein A or U1A antigen, and showed a measurable conductance change upon protein binding to the ligand. However, further work by the same group pointed to protein adsorption at the gold electrodes as the mechanism of sensing, as after passivation of the electrodes there was no longer any detectable conductance change upon protein binding [128]. *Star* et al. fabricated a SWNT-FET based DNA hybridization sensor and demonstrated detection of a single nucleotide polymorphism, a major cause of many diseases [129]. Similar work by *Tang* et al. showed that the mechanism of DNA hybridization detection on SWNT-FETs was that of hybridization on the gold electrodes, drawing into question the ability of SWNT-FETs to detect DNA hybridization [130]. Thus, many questions remain regarding the ability of SWNT-FETs to detect specific biomolecular interactions and as such any commercialization of this technology will happen only in the long term.

The most recent type of nanotube biosensor to be developed is based on semiconducting SWNT photoluminescence (PL). The science of carbon nanotubes photoluminescence is discussed in the contribution by *Lefebvre* et al. For biomedical applications, SWNTs have a number of advantages over conventional fluorophores; they fluoresce in a region of the electromagnetic spectrum where blood and tissue are most transparent, they will not photobleach and they are sensitive to changes in the local dielectric environment. *Strano* et al. adsorbed GOx and a reaction mediator, which quenched SWNT PL, to individually solubilized SWNT. Hydrogen peroxide produced by glucose oxidation would then react with the mediator and restore SWNT PL [96]. A DNA hybridization sensor was also fabricated by the same group, by first adsorbing a target DNA strand to the SWNT. Hybridization with the complement resulted in up to a 2 meV blueshift in the emission maximum [97]. Finally, addition of divalent metal cations to DNA-suspended SWNT resulted in a redshift of the SWNT PL. This was even detectable with the SWNT en-

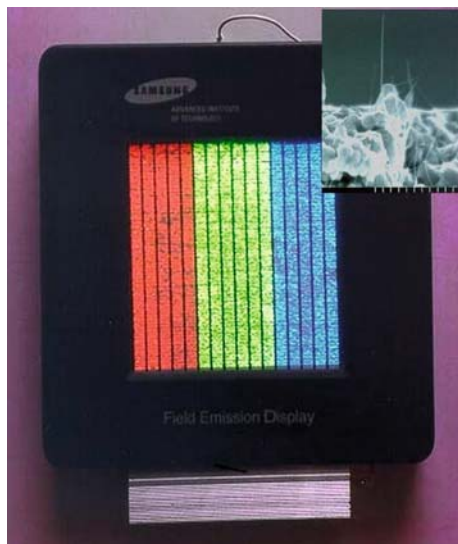
capsulated in living cells [98]. While the use of SWNT PL opens new avenues of sensing, any commercially available sensor is not expected to be available for  $> 10$  years.

In addition to the FET-based sensors that were described above, there have also been attempts to make sensors based on nanotubes functioning as electrodes, utilizing the field-ionization properties of nanotubes for gases. An example of this is the gas-ionization sensor, where the transition-metal state electrodes are replaced by arrays of nanotubes [131]. The sharp tips of nanotubes generate very high electric fields at relatively low voltages, lowering breakdown voltages several-fold in comparison to traditional electrodes, and thereby enabling compact, battery-powered and safe operation for such sensors. The sensors show good sensitivity and excellent selectivity, and are unaffected by extraneous factors such as temperature, humidity, and gas flow. These simple, low-cost, sensor electrodes based on vertically aligned MWNTs could be deployed for a variety of gas-sensor applications, such as environmental monitoring and in the chemical industry. Vertically aligned nanotubes, due to their high elastic compressibility, allow for building electromechanical pressure sensors. The resistivity measured in phase with the applied cyclic compressive strain on vertically aligned nanotube arrays has been found to be very sensitive to small strain levels [132]. Such strain sensors could be useful in MEMS devices. The response of the nanotube conductivity to pressure has also been utilized in flow sensing but the challenge remains in factoring out the effects of pressure alone (compared to temperature, adsorption, etc.) in influencing the nanotube conductance.

Electromechanical actuators have been proposed using sheets of MWNTs and SWNTs [133, 134]. Nanotube sheets infiltrated with polymer binders have been shown to perform as excellent electrochemical actuators, mimicking the actuator mechanism present in natural muscles. The nanotube actuators are superior to conducting polymer-based devices, since in the former no ion intercalation (which limits actuator life) is required. Several applications have been proposed including nanotube-based microcantilevers and artificial muscles that are stable at high temperatures. The electromechanical and electrochemical applications of nanotubes are being developed but face stiff challenges due to inherent limitations as well as competition from new ferroelectric and organic materials.

## 2.5 Carbon Nanotubes in Field Emission and Lighting Applications

CNTs have been considered as preferred field emitters due to their low threshold voltage, good emission stability and long emitter lifetime [135–138]. The contribution by *Ma et al.* discusses the electron relaxation processes in carbon nanotubes. These characteristics make them useful in the fabrication of cathode-ray lighting elements and flatpanel displays. The prototype cathode-ray tube (CRT) lighting elements using arc-derived MWNTs as cold electron



**Fig. 8.** A prototype 4.5 in FED using a printing method. Inset is an SEM image of single-wall carbon nanotubes projecting out of the nanotube layer. (Courtesy of Dr. W. Choi of Samsung Advanced Institute of Technologies)

sources exhibited stable electron emission, adequate luminance, and long life of the emitters [139]. Also, Samsung released the fabrication of a 4.5 in diode-type flat panel display using arc-based SWNTs [140] (Fig. 8). Even though SWNTs were shown to have excellent emitting performance [140], they were simply degraded at high emission current [141]. In this sense, DWNTs and or thin MWNTs have been examined as the best field emitting materials because they were shown to have a low threshold voltage comparable to SWNTs and a better structural stability compared to SWNTs, almost comparable to that of MWNTs [142–144]. Very recently, *Hiraoka et al.* [145] successfully fabricated a DWNT forest using Ni-based alloys with Cr or Fe as catalysts, and then measured the field emission from such a CNT/buckypaper cathode to an anode. They claimed that the homogeneous emission from the DWNT electrode is a result of the good electrical contact between the DWNTs and the grid substrate. Printable DWNT or thin MWNT-based field emitters are quite competitive for fabricating large-area FEDs (field emission displays) at relatively low cost. Even though technical problems have to be solved, it is certain that nanotube-based large-area color FEDs will appear on the market. This application seems to be clearly poised for commercial appearance in the next five years. The science of DWNTs is discussed in detail in the contribution by *Pfeiffer et al.*

Doping of nanotubes might also help field emission. *Chartier et al.* [146] have demonstrated experimentally and theoretically that B-doped MWNTs exhibit enhanced field emission (turn-on voltages at ca.  $1.4 \text{ V}/\mu\text{m}$ ) when com-

pared to pure carbon MWNTs (turn on voltages at ca.  $3\text{ V}/\mu\text{m}$ ). This phenomenon is thought to be due to the presence of B atoms at the nanotube tips, which results in an increased density of states close to the Fermi level. Theoretical tight-binding and *ab-initio* calculations demonstrate that the work function of B-doped SWNT is much lower (1.7 eV) than that observed in pure carbon MWNTs. Similarly, it has been demonstrated that bundles of N-doped MWNTs are able to emit electrons at relatively low turn-on voltages ( $2\text{ V}/\mu\text{m}$ ) and high current densities ( $0.2\text{--}0.4\text{ A}/\text{cm}^2$ ) [147]. More recently, individual N-doped MWNTs have also shown excellent field emission properties at 800 K; experimental work functions of 5 eV and emission currents of ca. 100 nA were obtained at  $\pm 10\text{ V}$  [148].

## 2.6 Carbon Nanotubes for Biological Applications

The optical properties of nanotubes impart promising advantages to their use in imaging applications within live cells and tissues. The unique photostability of SWNT photoluminescence allows for longer excitation time at higher laser fluence than either organic fluorophores or quantum dots. Also, in the range of 700–1400 nm, visibly opaque tissue exhibits greatly attenuated absorption, autofluorescence, and scattering characteristics. This range overlaps with the fluorescence profiles of many semiconducting nanotubes, allowing their observation in whole blood and thick tissue [149]. *Cherukuri* et al. [150] directly imaged nanotubes after incorporation by macrophages, observing no photobleaching – a phenomenon that plagues conventional biological imaging. Nanotube fluorescence was also used to image SWNT in tissue sections as well as measure their concentration in blood [151]. The extremely large resonance-enhanced Raman scattering profile of nanotubes is also available for detection in cells and can be applied to tissues as resonance enhancement occurs at near-infrared wavelengths [152]. The science of resonance Raman scattering is discussed in the contribution by *Saito* et al. Additionally, *Heinz* discussed Rayleigh scattering in carbon nanotubes, and *Hartschuh* discusses complementary techniques, such as near-field optics.

The therapeutic effect of drugs is constantly being increased through the development of new delivery vehicles. Previously, these vehicles included viral vectors, liposomes, cationic lipids, polymers, and nanoparticles. While viral vectors have an inbuilt transfection capability, there have been safety concerns surrounding their use, opening the door for other vehicles [153]. Although nonviral vehicles have versatility of shape, size and materials, one issue of concern is the poor penetration of some therapeutic agents into cells. Carbon nanotubes are readily internalized by cells; and after surface modification, they exhibit low cytotoxicity over the period of a few days [154–161]. In addition, they have a higher surface area to volume ratio than spheres, giving nanotubes the potential to be conjugated with more functional agents than spheres [159] and to accommodate higher loadings of therapeutic agents [161]. For these reasons, nanotubes have received a lot of attention as potential

vehicles for drug delivery. This section will address much of the work that has been done toward the successful use of carbon nanotubes to effectively deliver therapeutic agents into cells.

A suitable scheme to conjugate the drug and the nanotube is required to make CNTs into viable delivery vehicles. The nanotubes are hydrophobic and therefore insoluble in liquid biological media, so various methods have been exploited to functionalize the nanotubes, both covalently and noncovalently to make them soluble. In the noncovalent methods, molecules with hydrophobic groups, including RNA [157], DNA [162], Triton-X-100 [163], and 1-pyrenebutanoic acid [164], adsorbed reversibly to the nanotube surface, while the hydrophilic groups rendered the conjugates soluble. Covalent functionalization remains the more common method with various chemistries based on the creation of carboxyl [165, 166] and amino [159] groups on the ends and walls of the nanotubes. At the carboxyl sites, researchers have attached amine [159, 160, 167–169] and thiol [161] groups, to link various biomolecules [154–156, 158] to the nanotubes. Another critical step for nanotube drug delivery is to conjugate the nanotubes in such a way that the functionality of the biomolecules is maintained. The ability of covalently functionalized nanotubes to act as condensation sites for plasmid DNA has been demonstrated as a precursor to nanotube gene-delivery vehicles [169]. Proteins such as Biliverdin/Xbeta reductase enzyme have also been shown to form conjugates with functionalized nanotubes [163]. *Salvador-Morales et al.* [170] also report that nanotubes can activate a response in the complement, part of the human immune system, as evidenced by the adsorption of specific fibrinogen and apolipoproteins.

More recently, researchers have shown that nanotube conjugates can enter a cell and release the therapeutic agents for successful drug delivery. *Wu et al.* [159] reported the use of passive cellular uptake to deliver multiwall carbon nanotubes conjugated with amphotericin B (AmB), an antibiotic that is effective in treating fungal infections, but toxic to mammalian cells when it is free in solution. Functionalization of the nanotubes with AmB reduced the toxicity towards Jurkat cells, but still maintained (and in some instances increased) its functionality to inhibit visible growth of *C. parapsilosis*, *C. albicans*, and *C. neoformans*.

The introduction of foreign DNA to cells is another major area for therapeutic delivery using carbon nanotubes. *Cai et al.* [156] used nanotube spearing, utilizing the magnetic properties of nickel-embedded single-wall carbon nanotubes (SWNTs), to deliver DNA plasmid vectors containing the sequence for EGFP (a fluorescent protein) to Bal17 and Mouse splenic B cells, which are nondividing cells, and therefore notoriously difficult to transfect. They observed expression of EGFP in the cells, whereas a vector without EGFP did not show any detectable fluorescence. Furthermore, the use of a commercial product, Lipofectamine 2000, did not lead to any detectable fluorescence from EGFP, indicating the high efficiency of the nanotube-spearing method. *Cai et al.* also note that the small size of the nanotubes allows for penetration

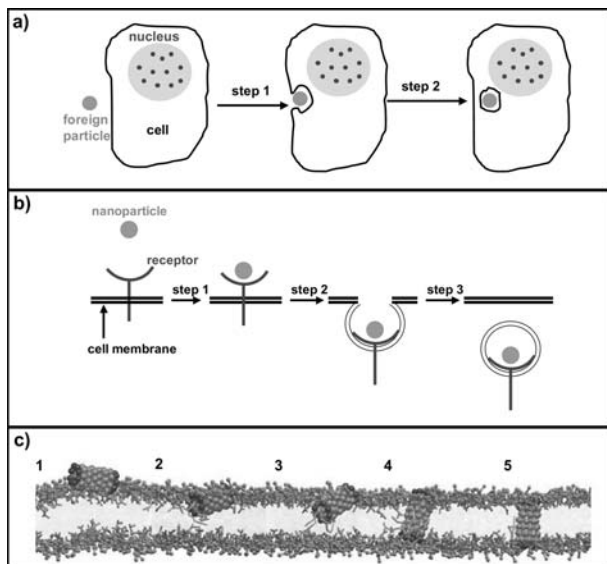
with only minor perturbations to the cell, and the magnetic spearing may be gentler than the ballistic method for mechanical delivery. Plasmid DNA vector-multiwall nanotubes have also employed a passive transport mechanism through the cell membrane, resulting in DNA uptake and gene expression of  $\beta$ -galactosidase in CHO cells [160]. Kam et al. [171] used this passive delivery mechanism, which led to the formation of endosomes containing oligonucleotide-single walled nanotubes, and followed with a second step to rupture the endosomes with pulses of a NIR (near-infrared) laser. Single-wall nanotubes absorb strongly at NIR wavelengths and exhibit local heating upon NIR absorption. This work showed that NIR radiation caused the nanotubes to release the DNA, allowing for its translocation into the cell nucleus. This technique was also used in the same study to cause cell death. Nanotubes were functionalized using a folate moiety that allowed them to be selectively internalized by cells that had been labeled with folate receptor tumor markers. Upon NIR irradiation, the cells were killed due to local heating caused by the nanotubes. In a separate study, Kam et al. [161] employed a technique that used a disulfide linker to conjugate oligonucleotide-SWNT and siRNA-SWNT. The conjugated nanotubes were passively endocytosed into the cell, and the disulfide bond was subsequently cleaved by the presence of thiol-reducing enzymes and the acidic environment in the liposome. The siRNA sequence they used caused silencing of the gene encoding for lamin A/C protein in HeLa cells, and they observed a transfection level that was twice as high as that of lipofectamine, a commonly used agent. Nanotubes have also been used to deliver proteins, such as cyt-c, to cells to induce apoptosis, or programmed cell death [69]. In this work, cyt-c-SWNT were endocytosed NIH-3T3 cells. The cyt-c-SWNTs were subsequently released by adding chloroquine to the cell medium, resulting in an increased rate of apoptosis.

While significant progress has been made in the area of carbon-nanotube delivery of therapeutic agents, there are still many issues left to resolve before clinical use of these materials can be realized. The field would be greatly advanced with the development of a noninvasive means to release nanotubes from endosomes into cells. Although passive methods allow for consistent uptake of nanotubes by cells, a controlled, yet nondestructive, method of nanotube transport with specificity to a target area would broaden the therapeutic potential for these materials. A more efficient means of unloading the cargo would also improve the efficacy. Further investigation is also needed to determine the long-term effects of conjugated nanotubes in-vivo, with issues such as toxicity, and interaction with biologic components like blood and tissue. Also of importance is the metabolism of these materials, and the possibility of in-vivo nanotube excretion after the therapeutic agent has been delivered. While these issues may take years to resolve, this field remains promising, with nanotubes already demonstrating high and versatile loading capacity for therapeutic agents, some selective cargo unloading, and better cell penetration than many other delivery materials.

For both biomedical applications mentioned above, the transport of nanotubes into cells is of central importance. The central question in the cellular transport of carbon nanotubes is the transportation mechanism. Understanding this process will help further drug and gene delivery, as well as enable precise cellular targeting for bioimaging applications. As yet, there exists a significant amount of controversy and confusion about the way in which nanotubes enter cells. In the case of SWNTs, *Dai et al.* [155] have reported that acid-functionalized SWNTs can enter the cells via the endocytosis pathway; however, *Bianco et al.* [160] suggests a passive, endocytosis-independent mechanism for ammonium-functionalized SWNTs and MWNTs. In the case of MWNTs, which are beyond the size limit of an endocytosis pathway, another suggested mechanism is one where the lipid molecules of the membrane are flipped, allowing entry into the cell [154, 172].

The coating on the nanotube surface is one factor that governs the nanotube–cell interaction. Serum in cell media contains various proteins, such as albumin, fibronectin and transferrin, that will adsorb to the nanotube surface. Even for systems without serum, the cell rapidly produces sufficient protein to coat the nanotube. These proteins are also present in vivo and almost immediately coat any foreign material introduced to the body. In either case, the actual surface presented to the cell is the protein-modified surface [173], and this has been confirmed in the case of gold nanoparticles [174].

The size and shape of a particle also affect the interaction of particles with cells. Phage cells in the primary immune system “eat” foreign particles (phagocytosis) that are above several hundreds of nm (Fig. 9a), and is one cellular uptake pathway suggested for CNTs [150]. Another potential mechanism is receptor-mediated endocytosis (Fig. 9b). For nanotube cellular transport, clathrin-mediated endocytosis is one of the most studied receptor-mediated pathways [175]. The molecular structure of clathrin is such that there is a natural size limit (about 150 nm) for the cages formed during endocytosis on the membrane, which suggests a size cutoff for particles [175]. Also, direct physical forces, including van der Waals, electrostatic, and hydrophobic effects that lead particles to be attracted to cells and affect the uptake process. For example, the presence of positive charges on a nanoparticle pushes the optimal wrapping size of the clathrin layer to nanoparticles larger than 25 nm [176]. If the adhesion free energy between the nanoparticles and the cell membrane is larger than that of typical receptor-ligand binding, the critical size of wrapping may also decrease [177]. However, MWNTs, that have a 10 nm radius and 200 nm length, are suggested not to have an endocytotic pathway, but possibly one of spontaneous switching of lipid molecules in the membrane (Fig. 9c) [160, 172]. Another unanswered question is the fate of nanotubes once they have entered the cell. For most biological applications it would be advantageous if the nanotubes were subsequently expelled from the cell; however, as yet this has not been reported in the literature. Much work is needed on nanotube cellular transport before these discrepancies will begin to be solved, allowing true understanding and control of nanotube placement



**Fig. 9.** (a) Phagocytosis of a foreign particle into a phage cell. *Step 1:* The membrane surrounds the particle. *Step 2:* The foreign particle is internalized. (b) Receptor-mediated endocytosis *Step 1:* A nanoparticle binds to a receptor on the cell membrane. *Step 2:* The receptor wraps the nanoparticle, forming an invagination on the cell membrane. *Step 3:* The nanoparticle is completely internalized into the cell. (c) Spontaneous lipid flipping *Step 1:* Spontaneous adsorption of a nanotube to the cell membrane. *Step 2:* The nanotube is partially inserted parallel to the membrane. *Step 3:* Random thermal fluctuations force one end of the nanotube toward the hydrophobic membrane core. *Step 4:* The end of the nanotube is directed, by the attached membrane lipids, to the opposite side of the membrane. *Step 5:* The final nanotube location is perpendicular to the plane of the lipid membrane (taken from [82])

inside cells. As such, using nanotubes for the aforementioned biological applications is not expected to yield any products for the foreseeable future and can be seen as a long-term project.

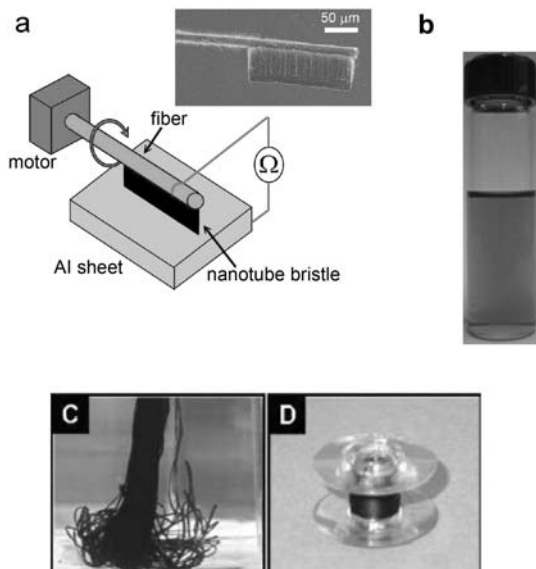
## 2.7 Carbon Nanotubes in Miscellaneous Applications

One of the applications of nanotubes that is in the market today is that of nanotube-based probe tips. With extremely small sizes, high conductivity, high mechanical strength and elasticity, nanotubes have shown their potential to be useful nanoprobes [178–180]. The nanotube-based tips provide better resolution for imaging and have better durability because of their elasticity, unlike conventional silicon tips that suffer from frequent tip crashes. Today, nanotube-based (mainly good-quality multiwall) AFM probe tips can be bought from scanning-probe instrument manufacturers. These still cost

dearly (few hundred dollars per tip) and can be considered as a low-volume specialty application. There have been lots of proposals for the use of nanotube tips in future technology, for example in imaging, nanolithography [181] and as nanoelectrodes. The nanotube tips have been used in the imaging of surfaces as well as biological species such as DNA at high resolution. The nanotube tips have the advantage that they are conducting, and they can be chemically modified for use in chemical imaging as well as in the manipulation of molecular species on surfaces. The future of nanotube probes will depend on how reliably these tips can be fabricated (either grown directly or transferred on to conventional tips) at high yield.

Another interesting application that has been touted for nanotubes is their use as membrane filters. Several groups have published papers in recent years suggesting that membranes made from aligned nanotube arrays (both SWNTs and MWNTs) could be used for selective transport of species [182–184]. Activated and porous carbons have been traditionally used as filters (e.g., water purification) but the advantage of nanotubes is that the pore sizes are very uniform and small, so that separation of really small molecules becomes possible. Although the pore size is small, the flow rate is not reduced due to the unique nature of the flow of solvents through the nanotube cavities. Another advantage could be that the nanotube surfaces may be chemically modified to make the separation very selective. Although several groups are working to develop nanotube-based membranes for filtration, molecular as well as gas separation, these are still far from commercial products and their development could take more than a decade.

In recent years, work has progressed in getting stable dispersions of nanotubes in various solvents (nanotube inks) [185] (Fig. 10), which can be directly spun or printed onto various substrates. Easily printable (e.g., inkjet printing) circuits and films are extremely useful for a range of applications ranging from flexible electronics to antennas. Nanotubes have also been spun into fibers using various techniques ranging from extrusion of nanotube slurries to drawing from aligned arrays. High weight percentage dispersions of SWNTs have been spun directly or using polymer binders to continuous fibers reaching macroscopic lengths [186, 187] (Fig. 10). The fibers can be also assembled into sheets, membranes and other products. Several applications have been demonstrated for such nanotube fibers and their products, for example as high-brightness incandescent bulbs [188], reinforcements in polymers, shielding elements and in ballistic protection. Direct growth of aligned nanotubes can be used to make distinct products, such as brushes [189] (Fig. 10). The tiny brushes with nanotube bristles have been demonstrated for use in a variety of applications including cleaning of microscale spaces, conducting contact brushes, and probe arrays. Another possibility is the use of aligned nanotube arrays as dry adhesive tape; one recent study shows that properly engineered nanotube arrays could have adhesive strengths even rivaling gecko feet [190]. The variety of assembled and dispersed products from nanotubes could feed various industrial applications in the future and could allow



**Fig. 10.** A few miscellaneous applications that have been demonstrated using nanotubes. (a) Nanotube-based microbrushes have been synthesized and can be used in various instances including as a brush contact (seen in the schematic). (b) Nanotube inks: fully dispersed SWNTs in water, using a surfactant. Such dispersions in water or organic solvents and polymer binders have been used for printing structures using inkjet printers on various substrates, for example to make conducting nanotube lines. (c,d) Fibers of nanotubes and polymers have been spun in a continuous fashion. The SEM images show SWNT-PVA fibers that have been spun using a coagulation-based spinning method [191]. These nanotube-polymer fibers could be useful in composites, membranes, etc.

continuous and roll-to-roll manufacturing incorporating nanotubes. Many of these products (in particular the spun fibers) could come to the marketplace within the ten-year time frame.

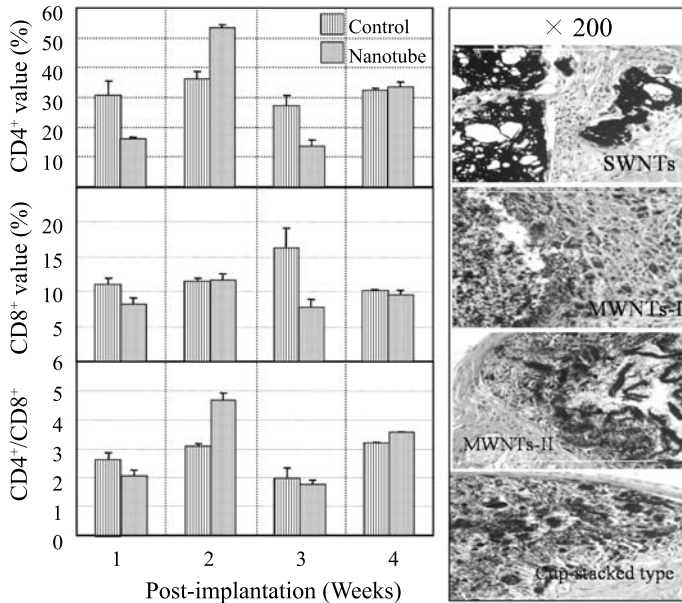
Research on carbon nanotubes has also provided avenues in developing novel carbon nanostructures, which could have specific applications. Nanotubes filled with various materials have been made using approaches such as capillarity infiltration [192, 193]. Hybrid nanowire–nanotube structures have been designed and even branched nanostructures have been synthesized [194, 195]. All these structures provide the range of building blocks that could one day be used in nanotechnology applications, but these are clearly beyond the ten-year time frame we have considered. However, there are some structures, such as carbon nanohorns (larger fullerene-like structures with low density and high surface area) as described in detail in the contribution by *Yudasaka et al.* [196] that have been shown as useful in applications related to electrodes and supercapacitors and a variety of other applications.

These materials can be easily produced in bulk by the pyrolysis of carbon precursors and could be commercialized within the ten-year period. Additionally, *Yudasaka et al.* discuss in this volume the science and application of nanohorns, *Tenne et al.* discuss inorganic nanotubes, and *Charlier et al.* discuss the science of graphene.

## 2.8 Environmental and Health Effects of Carbon Nanotubes

As we have seen in the previous sections, carbon nanotubes hold great potential in electronics, environment, energy, and bio/medical fields. One uncertain issue that still remains unsolved is the safety and biocompatibility of the nanotube material [197–205]. Recently, it has been suggested that a simple and effective method can be used to evaluate the toxicity and biocompatibility of carbon nanotubes through a measurement of CD4<sup>+</sup> and CD8<sup>+</sup> T-cells in peripheral blood and their histopathological study on carbon-nanotube-implanted tissues [201] because CD4<sup>+</sup> (a coreceptor for MHCII) and CD8<sup>+</sup> (a coreceptor for MHCI) give us important antigen information of T-cells. Interestingly, in the protocol demonstrated, the mortality of animals was negligible, and no chronological changes of body weight were observed among nanotube-implanted mice versus control over three months postimplantation (Fig. 11a). Time-dependent changes in peripheral T-cells, which involved into carbon nanotubes in situ, were well correlated with a processing phase of granuloma formation (Fig. 11b). Even though their potential toxic nature was probed to be significantly lower for CVD-grown MWNTs, more detailed and systematic (long-term) studies with regard to the toxic natures of various types of carbon nanotubes (including direct aspiration of the tubes in lungs) have to be carried out to address the safety of carbon nanotubes.

Nanotube cytotoxic properties appear situational, depending highly on the degree and type of functionalization, aggregation state, and the presence of metal-catalyst particles remaining from synthesis. Pristine nanotubes are reported to cause oxidative stress and decrease cell viability [206,207], though there is some indication that leftover catalyst particles contribute to this effect [208]. The cytotoxicity can be greatly attenuated via functionalization. *Sayes et al.* [209] reports that the high cytotoxicity of pristine SWNTs can be reduced to zero with increasing coverage with a covalently attached polar functional group. The choice of functional group can impart a range of cell responses including the activation of primary immune cells by polyethylene glycol-coated SWNTs [210]. The toxicity of noncovalently functionalized carbon nanotubes similarly depends on the nature of the adsorbate. Successfully individually encapsulated DNA-wrapped SWNTs leave cells viable upon internalization of the complex [211]. Toxicity studies are also reported in the contribution by *Terrones et al.* on nitrogen doped nanotubes.



**Fig. 11.** (a) Time-dependent changes in CD4<sup>+</sup>, CD8<sup>+</sup> and CD4<sup>+</sup>/CD8<sup>+</sup> after the subcutaneous implantation of high-purity carbon nanotubes, (b) light microscopic pictures of skin tissue after three months implantation of SWNTs, MWNTs-I, MWNTs-II and cup-stacked-type carbon nanotubes, respectively (from [201])

### 3 Conclusions

It is important to summarize the applications of nanotubes in terms of the timeline we discussed in the beginning of this chapter. In addition, it would be useful to separate applications that rely on large-scale manufacturing (bulk applications) from those that are based on controlled fabrication. We will discuss the challenges, that are involved in the successful transfer of knowledge to commercial applications. The great promise with which nanotubes has fascinated the scientific and technological community needs to bear fruit at this juncture. For this to happen, it is important to address the realistic potential of nanotubes as a commercial commodity. In Table 2 we group the applications of nanotubes, that we discussed in earlier sections, in two categories; one, based on the timeline of commercialization and two, based on their scale (bulk vs. limited volume).

It would seem incomplete if we do not discuss some of the issues and challenges that have faced carbon-nanotube applications from the very beginning. These challenges have slowed down the pace of nanotube commercialization. The foremost among these is the manufacturing issue. The bulk applications of nanotubes necessarily will rely on the ability to manufacture nanotubes in high volume, on the industrial scale. For the case of CVD-grown MWNTs

**Table 2.** Shows applications of nanotubes grouped as present (existing), near term (to appear in the market within ten years) and long term (beyond ten-year horizon) and as categories belonging to bulk (requiring large amounts of material) and limited volume (small volume and organized nanotube structure) applications

	Large-volume applications	Limited-volume applications (mostly based on engineered nanotube structures)
Present	<ul style="list-style-type: none"> <li>– Battery electrode additives (MWNT)</li> <li>– Composites (sporting goods; MWNT)</li> <li>– Composites (ESD* applications; MWNT)</li> </ul>	<ul style="list-style-type: none"> <li>– Scanning probe tips (MWNT)</li> <li>– Specialized medical appliances (catheters) (MWNT)</li> </ul>
Near term (less than ten years)	<ul style="list-style-type: none"> <li>– Battery and supercapacitor electrodes</li> <li>– Multifunctional composites (3D, damping)</li> <li>– Fuel-cell electrodes (catalyst support)</li> <li>– Transparent conducting films</li> <li>– Field emission displays/lighting – CNT-based inks for printing</li> </ul>	<ul style="list-style-type: none"> <li>– Single-tip electron guns</li> <li>– Multitip array X-ray sources</li> <li>– Probe array test systems</li> <li>– CNT brush contacts</li> <li>– CNT sensor devices</li> <li>– Electromechanical memory device</li> <li>– Thermal-management systems</li> </ul>
Long term (beyond ten years)	<ul style="list-style-type: none"> <li>– Power transmission cables</li> <li>– Structural composites (aerospace and automobile, etc.)</li> <li>– CNT in photovoltaic devices</li> </ul>	<ul style="list-style-type: none"> <li>– Nanoelectronics (FET, interconnects)</li> <li>– Flexible electronics</li> <li>– CNT-based biosensors</li> <li>– CNT filtration/separation membranes</li> <li>– Drug-delivery systems</li> </ul>

\* ESD stands for electrostatic discharge

(so-called Endo fibers) large-scale manufacturing has been reasonably successful. Companies such as Hyperion in the USA and Mitsui Corporation and Showa-denko in Japan have built manufacturing facilities that can produce up to a hundred tons of material per year. This has happened over the last decade and in particular the last few years, essentially to supply the demand for nanotubes arising mainly from the ESD and battery applications. Even this volume is tiny in comparison to carbon fibers and other carbons that are commercially used. In the case of SWNTs the situation is not the same. Even after a decade and a half of research in this area, no technique can yet manufacture this material in reasonable volume. The amounts are still restricted to gram quantities, limiting any real bulk application for the material. There have been bold undertakings by several companies in the USA, Canada and China recently promising a SWNT supply in comparable

volumes to the MWNT availability in the next decade or so, but these claims remain to be demonstrated. In addition to availability there are also other issues such as cost (SWNTs still sell at around 100 USD per gram, compared to a few dollars/kg for the CVD-grown MWNTs) as well as fundamental materials-science problems and compatibility. For example, we have already discussed the issue of interfaces when we discussed polymer composites and more work needs to be done in engineering to solve these problems. In the meanwhile, the promising applications in the near term will come from value-added uses, such as application of nanotubes as additives in battery electrodes to help mechanical stabilization.

For applications that require organized nanotube structures there has been a clear lack of emphasis on integration schemes. The revolutionary applications of nanotubes, for example nanotube electronics, need much more focus on controlled assembly and integration. There are still holy grails in this path, for example the selective growth of nanotubes with specific chirality or diameter. There are still challenges in obtaining nanotubes with controlled length, precise alignment, control of location, etc. Processing is also an issue. For example, the temperatures that are used to grow nanotubes today are far higher than what is acceptable in today's silicon semiconductor processing and hence integration of nanotubes into existing processes in the industry is challenging. Perhaps such high-value applications with nanotubes will take several more decades to happen. In the near term, there could be nanotube-based devices in more forgiving applications such as field emission displays, sensors, membranes, coatings, etc. Good examples are the electromechanical memories and transparent conductive films that are based on random assemblies of nanotubes. For even these to be commercially viable, they need to be manufactured with consistency and in a cost-effective manner, so that they compete with other material choices available in the market. The contribution by *Joselevich et al.* gives a survey on the synthesis and processing of carbon nanotubes.

There are also other issues that need to be carefully considered as we go ahead with applications of nanotubes. Of utmost importance are the environmental and health-safety issues related to nanomaterials. There simply have not yet been enough studies that could unequivocally prove either way (regarding safety) and for all practical purposes the jury is still out. Isolated experiments have shown that the nanotubes are not toxic. Whatever is the final word, we need to be aware of protocols on how to handle these materials, both in the laboratory and in an industrial setting. Well-defined regulatory controls need to be in place when large quantities of the material are handled routinely. The long-term impact of these on health should be studied. There needs to be standard procedures established on how to package and transport nanotube materials and how to handle them.

The next decade will be the decade of nanotechnology thus requiring research in nanometrology (see contribution by *Jorio et al.*). Carbon nanotubes and their products will have a seminal role to play. Large amounts of

resources have been invested for understanding and developing the carbon-nanotube material. The last several years have been extremely exciting. The new scientific discoveries and new knowledge base developed with nanotubes have been enormous and satisfying. We are now at the critical juncture where the demonstrations of applications need to get translated into product lines. Some of these endeavors will be successful and some will fail. The test for the nanotube material will be whether it will live up to the expectations and promises that have been flouted based on its amazing physical properties.

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