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Introduction to carbon nanotube and nanofiber smart materials

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Abstract

The potential use of carbon nanotubes and nanofibers as smart composite materials is discussed in this paper. An overview of the properties of carbon nanotube materials is presented, and then four applications under development are briefly discussed. The first application is electrochemical actuation in dry and aqueous environments. The second is a carbon nanotube polymer piezoresistive strain sensor developed for structural health monitoring. Third, nanotubes are used with an electrolyte for harvesting power from structural vibration. Fourth, a carbon nanotube bioelectronic sensor is discussed. Tying all this together, a vision is presented for using nanoscale smart materials to synthesize intelligent electronic structures with prescribed elastic and electrical properties for a wide range of new applications. Hurdles to be overcome to achieve this goal are also discussed.

Keywords: A. Nano-structures; B. Elastical properties; D. Electron microscopy; E. Casting

1. Introduction

Smart materials are solid-state transducers that have piezoelectric, pyroelectric, electrostrictive, magnetostrictive, piezoresistive, electroactive, or other sensing and actuating properties. Existing smart materials such as piezoelectric ceramics, electroactive polymers, and shape memory alloys have various limitations holding them back from practical applications. The limitations center on the requirement for high voltage or high current, or the material is brittle, heavy, or has a small range of strain or force actuation. Smart nanoscale materials may reduce these limitations and represent a new way to generate and measure motion in devices and structures. Among the various nanoscale materials, carbon nanotubes (CNTs) exhibit extraordinary mechanical properties. For instance, CNTs are the strongest and most flexible molecular material known due to the unique C–C covalent bonding and seamless hexagonal network. The nanotubes also have electrical conductivity or semiconductivity, and high thermal conductivity in the axial direction [1–3]. The discovery of Multi-Wall Carbon Nanotubes (MWNTs) by Iijima [4] and the C60 fullerene and single wall carbon nanotubes (SWNTs) by Benning et al. [5] opened the possibility for a new class of smart materials based on nanoscale materials. Structural and electrical characteristics of CNTs make them promising for developing unique and revolutionary smart composite materials. In addition, unlike other smart materials, CNTs have high strength as well as high thermal and electrical conductivities, and 'therefore' can provide structural and functional capabilities simultaneously, including actuation [6–8], sensing [9–11], and generating power [12]. These capabilities represent the possibility for developing actuators capable of high stress and high strain operating at low voltage, and multi-functional electrochemical and mechanical sensors.

This paper discusses four applications of CNTs that are under development at the University of Cincinnati. The first application is the CNT electrochemical hybrid composite actuator working in a wet and dry environment [13–16]. The second application is the CNT piezoresistive sensor for use in a biomimetic Artificial Neural System (ANS) for large structures

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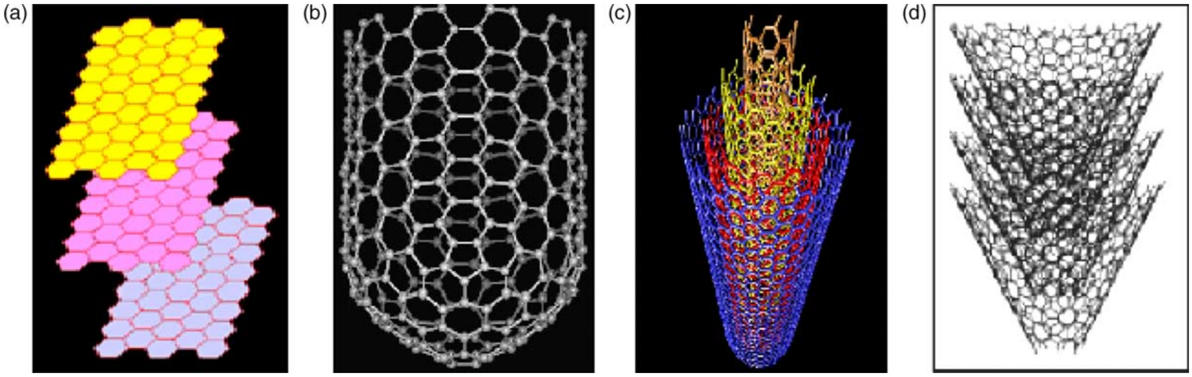


Fig. 1. Schematic illustration of CNTs: (a) carbon nano-walls (figure from [21]); (b) arm-chair type metallic SWNT (10, 10) (figure from [22]); (c) structure of multi-walled nanotube (figure from [23]); and (d) structure of a four-nanocone-stacked CNF (figure from [24]).

[17]. Third, is applying the voltage generation property of a CNT composite for power harvesting for a vibrating structure [18]. The fourth application is a bioelectronic sensor. Materials for all of these applications have been built and tested based on Carbon Nanotube (CNT) and Carbon Nanofiber (CNF) composites. The CNF material is 100 times lower in cost than single wall carbon nanotubes, making the applications discussed feasible based upon the current material cost.

2. Carbon nanotube and nanofiber materials and properties

There are three common types of CNT raw materials that can be used as smart materials. These are Single Wall Carbon Nanotubes (SWNT), Multi-Wall Carbon Nanotubes (MWNT) and Carbon Nanofibers (CNF). The three materials can also be used in combination to develop intelligent materials. The morphologies of these materials are shown in Fig. 1 [19–32]. These nanotube materials are commercially available [3,29,32], and they can also be synthesized using commercial Chemical Vapor Deposition (CVD) systems. A unique facility to grow SWNT and MWNT using a computer controlled CVD nanofurnace is available [19,20].

A summary of the characteristics of each of these nano materials is given in Table 1. Nanotube properties are discussed in [21–24]. The nanotube electronic property is a strong function of its atomic structure, mechanical deformation and chemical doping. Changing these properties can induce strong changes in electrical conductance of the nanotube [25]. The electrical impedance of CNTs was shown to be very sensitive to chemical exposure [26,27] and mechanical deformation [28]. The properties depend on the type of nanotube [29–32].

The properties of CNT are important to understand for designing smart composite materials and are discussed in Sections 2.1–2.9. Properties of nanotubes and nanostructured materials are discussed in [33–63].

2.1. Elastic and thermal properties

Nanotubes are the stiffest known fiber, with a measured Young's as high as 1–1.4 teraPa [2,58]. The tensile strength is

Table 1
Designation of carbon nanotubes and nanofibers

Material type	Typical characteristics
Single wall carbon nanotubes (SWNT)	SWNTs have excellent mechanical and electrochemical properties. Incorporating SWNT into polymers at high loadings is difficult. SWNT have a wall one atom thick and diameters typically 1.4 nm [29] but range 0.3–2 nm, are 200+ nanometer length; grown by catalyzed chemical vapor deposition (CVD), cost purified is ~$500/g. (Carbon Nanotechnologies, Inc., [3])
Multi-wall carbon nanotubes (MWNT)	MWNTs have multiple walls and diameters of 10 nm and larger. They have good electrochemical properties, the cost is moderate, and incorporating the nanotubes into polymers may be possible by growing arrays of nanotubes and casting the polymer around the arrays. The MWNT do not have as high or varied properties, but are easier to process because of their larger diameter [30,31] of 10–50 nm, and 1–50 μm length, grown by CVD; also bamboo MWNT 20–40 nm diameter, 1–20 μm length, internal closeouts, ~$150 g (First Nano, Inc.,) The double wall CNT are a variation of MWNT. Size is 2–4 nm diameter, 1–50 μm length, grown by CVD of methane over cobalt nanoparticles supported on porous MgO nanoparticles. (Nanolab, [29])
Carbon nanofibers (CNF)	CNFs have moderate electrochemical properties and incorporating CNF into polymers is easier because the fibers are large. CNFs have multiple concentric nested tubes with walls angled 20° to the longitudinal axis. While CNF are similar to large diameter MWNT, CNF are not continuous tubes and their surfaces show steps at the termination of each tube wall. The nanofibers include PR-24 (~65 nm diameter) and the PR-19 (~130 nm diameter). The PR-19 have a CVD layer with a turbostratic carbon layer parallel to the surface and these fibers may be more robust to breakage, but the electrical properties of the nanofiber are changed by the coating. The PR-24 does not have a CVD coating. There are low and high density variations of these two nanofiber types [32], 50–100 μm length;, vapor grown carbon fiber (VGCF), different grades: $100/lb: PR-24; PR-19. (Applied Sciences, Inc., [32])

50 GPa or above [3]. Compared with carbon reinforcing fibers, the strength to weight ratio of nanotubes in the axial direction is up to four times greater [56]. The maximum strain of SWNT is $>10\%$, which is greater than most structural materials. These strong mechanical properties are due to the C–C covalent bonding and the seamless hexagonal network. Thermal conductivity is also very high in the direction of the nanotube axis, typically about 1750–5800 W/mK [33,59].

2.2. Electrical conductivity

Electronically, the carbon nanotube can be either metallic or semiconducting, depending on the chirality. Carbon nanotubes also have been predicted to conduct current ballistically without dissipating heat. The conductance (the inverse of resistance) of SWNTs is predicted to be $2G_0$ independent of the diameter and length, where $G_0=2e^2/h=1/(12.9\ \mathrm{K}\ \Omega)$, which is one unit of the conductance quantum, and e, h are the charge on one electron and Plank's constant, respectively [34]. Temperature and magnetic fields affect the resistance of the nanotubes. Metallic SWNT behave as long ballistic quantum conductors with the charge carriers exhibiting a large phase-coherence length and it has the strongest electrochemical properties possibly because the lower resistance allows a greater double layer charge buildup. Ropes have been measured with a resistivity of 10–4 Ω-cm at 300 K [60], making them the most conductive fibers known. Individual tubes have been observed to conduct electrons with no scattering, with coherence lengths of several microns [61]. In addition, they can carry the highest current density of any known material, measured [62] as high as 109 A/cm^2.

2.3. Magnetoresistance

The CNT also have spin-dependent transport properties or magnetoresistance [35]. The direction of magnetization of the ferromagnetic electrodes used to contact the nanotube defines the spin direction of the charge carriers into and out of the nanotube and a change in the resistivity of the nanotube. Spintronic nanoscale devices in theory can be built using the superconductivity and magnetoresistance effects, where the nanotube-metallic junction appears to have a strong effect on the spin-dependent transport. The magnetoresistance effect is interesting, but seems difficult to use for sensing strain of the nanotube and for use in a smart composite material.

2.4. Piezoresistance

A pioneering experiment showed that the conductance of a metallic CNT could decrease by orders of magnitude when strained by an atomic force microscope tip [28]. It appears that the band structure of a carbon nanotube is dramatically altered by mechanical strain and that the conductance of the CNT can increase or decrease depending on the chirality of the nanotube. The strain changes the structure of the quantum states available to the electrons. Metals conduct electricity easily because their electrons have easy access to the quantum states that carry the electrons long distances. These states are in the conduction band of the electronic structure. In semiconducting nanotubes, there is a band gap, which is an energy barrier that electrons must overcome to reach the conduction band. The extra energy push to overcome the band gap can come from heat or an electric field or strain. Actually, strain changes the band structure, which changes the electrical properties making the nanotube more or less conductive (piezoresistive) depending on the chirality of the nanotube. The piezoresistance effect is promising for sensing.

2.5. Electrokinetics of nanotubes

In fluids, ponderomotive responses of particles can be produced by externally applied time-dependent electrical fields [37,38]. The electrical properties (conductivity and dielectric constant) of a nanotube are usually different than of the fluid. Therefore, when a nanotube is in an electrolyte, it will attract ions of opposite electrical polarity forming an electrical double layer. If a uniform DC electric field is applied to nanotubes suspended in an electrolyte, the electrical double layer surrounding the nanotube is distorted, and electrical charges that define the nanotube's structure are induced to appear at the interfaces. The distortion of the electrical double layer and the creation of interfacial charges is what gives the nanotube an electric dipole moment and allows the nanotube to be moved in an electric field. The forces are small when considering smart material applications.

2.6. The piezoelectric property

In CNT, the piezoelectric effect is very small based on theory [63]. Therefore, using piezoelectric nanotubes/wires/ribbons currently seems less promising than using the electrochemical property of CNT for developing high strain smart nanocomposite materials. Non-carbon nanotubes have small piezoelectric properties.

2.7. The electrochemical effect

Introducing excess charge into CNT produces mechanical deformations that do mechanical work [6]. The charge injected into the valence or conduction band causes the electronic structure to shift. The electrochemical effect should produce up to 2% strain based on the basal plane intercalation strain of graphite. The electrochemical property can generate large strains/forces using low voltages. Therefore, the electrochemical property of CNTs is considered promising for actuation.

2.8. Telescoping nanotubes

The MWCNT have been proposed to be used as rotational and translational bearings, and as a nut and screw for building nanomachines [39–41] by taking advantage of the spiral chirality of nanotubes. A screw actuator and worm gears are other ideas that come to mind, but forming nanotubes with commensurate shells or putting defects into the nanotubes to form the threads is difficult, particularly for large force macroscale actuators. Instead, a telescoping carbon nanotube actuator seems a possible device. Electrical charge may be used to telescope the actuator and van der Waals force and opposite electrical charge might be used to retract the actuator. The actuation forces are being modeled but the actuation has not been verified experimentally yet. In addition, the resistance of the nanotube depends on the telescoping length. This indicates that the telescoping can be used as a displacement sensor that is nanoscale in size. This type of sensor may have applications in the areas of structural health monitoring of crack initiation and measuring displacements and voltages in biological systems.

2.9. Power generation

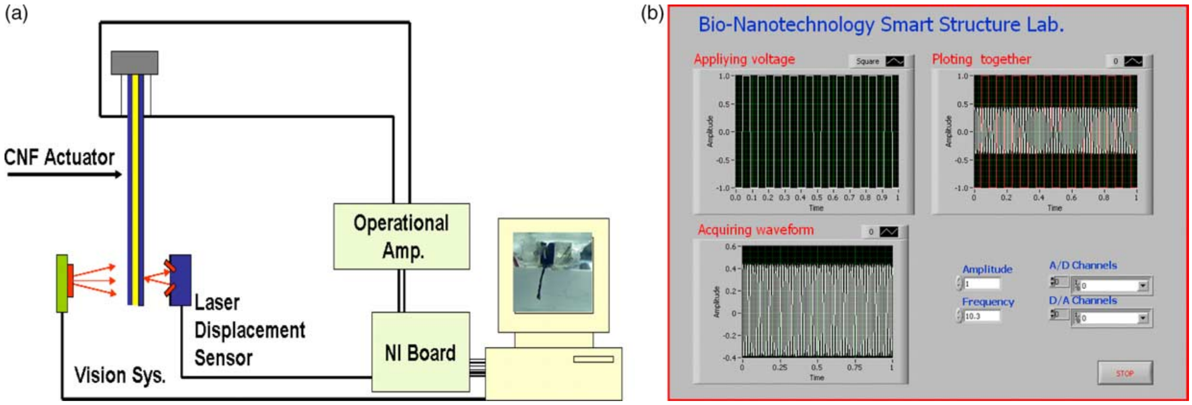
This property is due to ionic flow over the nanotube surface. A coulomb drag property causes charge to flow in the nanotubes in an electrolyte. The current flow depends on the ionic fluid and flow velocity [42]. The power generation is small, but is promising for medical applications and flow sensing because it continuously produces power based on flow only.

The properties (Sections 2.1–2.9) discussed above have the potential to form unique smart composite materials. The following sections discuss some initial efforts at making smart materials using nanotubes and nanofibers. These results are all recently obtained, and the field of nanoscale smart materials itself is new and in an emerging stage.

3. Nanofiber and nanotube hybrid electrochemical actuators

Actuators change electrical or electrochemical energy into mechanical energy and ideally produce high power using a small volume of material. Researchers in the area of smart structures have been trying since about 1987 to overcome the limitation of either the small strains or small forces produced by smart materials. It is apparent that there is a need for a structural actuator material that has an intermediate load bearing capability and also an actuation capability between that of artificial muscle and piezoelectric materials. With the help of nanoscale materials like CNT, there is the potential to develop new actuators that will provide higher work per cycle than previous actuator technologies, and generate higher mechanical strength. In addition, CNTs offer high thermal stability, and this actuator might be used in higher temperature environments. The first actuator made of CNTs was a macroscale sheet of nanotubes termed 'buckypaper' which is composed of highly entangled SWNT bundles formed by van der Waals attraction [6,43,44]. This actuator produced strain due to the change in dimension of the nanotube in the covalently bonded axial direction caused by an applied electric potential. The charge injection leads to a change in the dimension of the nanotube paper causing the assembly to bend. This excess charge is compensated at the nanotube–electrolyte interface by electrolyte ions forming a double layer.

In 2004, CNF hybrid actuators were developed [13–15] with good electrochemical actuation properties and increased strength and stiffness, but these properties are still far below the properties of individual nanotubes. Recently CNF/PMMA (polymethyl methacrylate) polymer based hybrid actuators working in aqueous electrolyte and with a solid polymer electrolyte (SPE) in air were tested [15]. The SPE enables operation in a dry environment instead of liquid electrolytes. Furthermore, the nanotube actuator performance was improved for structural applications by constructing and testing a SWNT–epoxy layer electrochemical actuator [16]. This actuator material has large strain with increased stiffness. Fig. 2(a) shows an experimental test bed developed to characterize and measure the displacement of the actuators using a laser displacement sensor (Keyence, LC-2400 Series), National Instruments PCI board, and a specially designed operational amplifier to apply forces with frequencies ranging from 0.2 to 5 Hz. Fig. 2(b) shows the data acquisition program designed within a LABVIEW VI to control the experiment. This system simultaneously provides the actuation signal, a laser measures the displacement, and a video camera captures the response of the actuator. The actuators are tested in a 2 M NaCl solution to demonstrate the performance. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) are carried out to characterize the electrochemical properties and power required to operate the actuator.



Amplitude 1
Frequency 10.3
A/D Channels 0
D/A Channels 0

Fig. 2. The electrochemical actuation experimental set-up: (a) electrochemical actuation characterization and control system; and (b) designed LABVIEW VI.

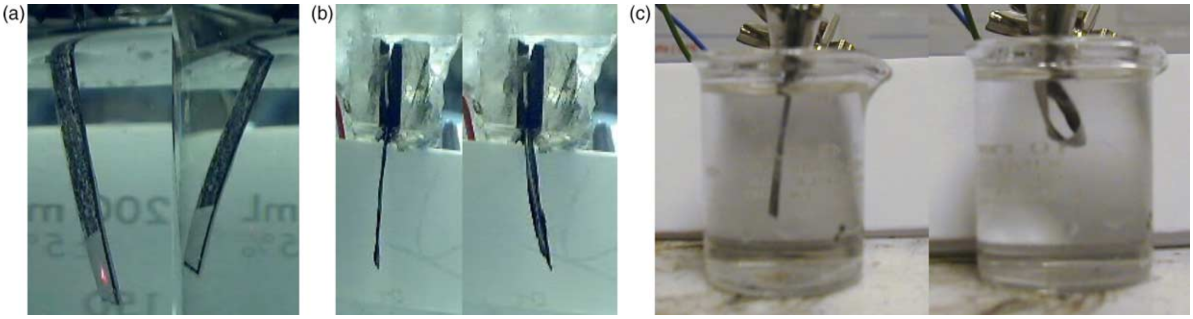


Fig. 3. Bending motion of: (a) CNF composite-3M tape in the electrolyte solution; (b) CNF/SPE/CNF dry actuator; and (c) SWNT–epoxy layered actuator due to a steady high voltage (10 V) for a long period (minutes).

The aqueous actuation of a CNF–PMMA composite strip in electrolyte is shown in Fig. 3(a). The bending occurs mostly near the top of the actuator. This is because of agglomeration of the CNF in the polymer and shunting in the electrolyte, and because the resistance of the actuator reduces the voltage in the lower part of the actuator. Still, the actuator produces a large actuation at 15 V. Fig. 3(b) shows the deflection of (a) CNF-based bimorph dry actuator when a voltage is applied between the two CNF electrodes (CNF actuators). In order to develop the carbon nanotube electrochemical actuator working in air, PMMA based SPE films made of ion exchange materials in different mole ratios were prepared by the solution casting technique. Fig. 3(c) shows a SWNT–epoxy layered actuator after applying 10 V for a period of minutes. After applying a high voltage, the displacement became very large and the actuator curled and it was not reversible. A high voltage will cause a large current that may burn the nanotubes or heat the epoxy above the glass transition temperature, although the electrolyte will act to cool the actuator in this case. The SWNT–epoxy actuator is being developed for dry actuation.

Fig. 4(a) shows the deflection results for the CNF–PMMA composite actuator. With an increase of the frequency of the square wave, deflection of the cantilever beam actuator decreases. Also, with the increase of potential, the deflection of the cantilever beam actuator increases. Higher potential causes greater charge accumulation at the CNF/electrolyte interface and causes the faster response and higher strain. Fig. 4(b) shows the relationship between the deflection of the dry CNF actuator and the voltage applied. The applied potential influences the strain rate in electrochemically driven CNF dry actuators. Overall, these results have verified that increasing the magnitude of the applied potential increases the strain rate and the material behaves as a smart material. The CNF dry actuator has a lower bandwidth because the actuator is not hydrated, thus the actuation is slower and the amplitude is small compared to the wet actuator. Fig. 4(c) shows the deflection results due to the square wave potential applied to the CNT–epoxy layered composite actuator. The deflection of the layer actuator increases as the applied potential increases and is also in the lower frequency range. As shown in Fig. 4(c), the deflection is one directional, reversible, and generates a high strain rate.

To summarize this section, in the SWNT the van der Waals forces do not provide efficient shear transfer for smart structures applications. The focus of the work was to develop a host polymer for nanotubes/nanofibers to provide simultaneous actuation and structural strength. Carbon nanofibers were tested because of their low cost. The experimental results and EIS testing verify that the electrochemical CNF–PMMA hybrid actuator is a new smart composite material. For the first time, it has been shown that CNFs have good electrochemical actuation properties based on the wet actuator results. Then, for wider applications, a CNF based dry actuator was fabricated using a solid polymer electrolyte and tested. Compared to previous SWNT buckypaper actuators, the dry-based CNF actuator does not require a liquid for operation, but a higher actuation voltage is needed. A wet actuator was also formed using MWCNT and epoxy. Because of the potential for incorporating the CNT/CNF into stronger polymers, and the use of improved or solid oxide electrolytes, large structures that actuate may become feasible.

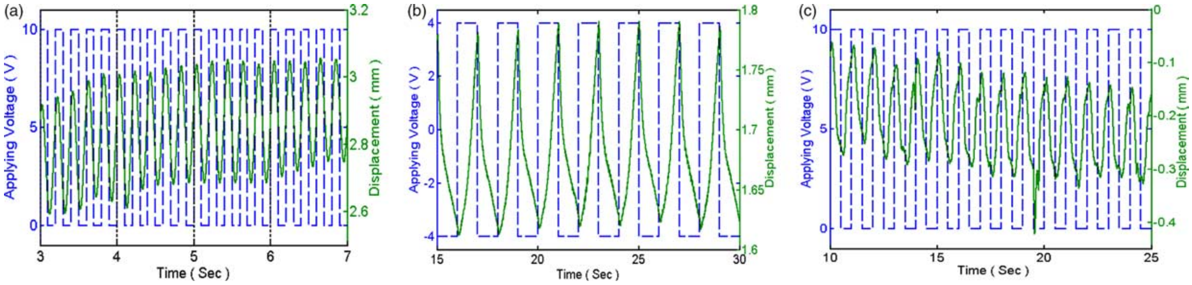


Fig. 4. Actuator deflection due to a square wave input: (a) wet composite actuator with an input of 10 V at 5 Hz; (b) dry actuator due to an input of ±4 V at 0.5 Hz; and (c) CNT—epoxy layered actuator due to a 10 V input at 1 Hz.

4. Nanotube strain sensors

The structural and electrical characteristics of Carbon Nanotubes (CNT) make them a promising smart sensor material. The high strength, large elastic modulus, and piezoresistivity (resistance changes with strain) indicate the possibility to make a long continuous sensor to measure strain over a large structure for Structural Health Monitoring (SHM). Previous research has considered two approaches for strain sensing using CNT. These are Raman spectroscopy, and piezoresistive buckypaper strain sensing. Because of the small size of nanotubes, several studies of the strain sensing properties of CNTs at the nanoscale [45] and macro-scale [46–48] were performed using Raman spectroscopy. However, Raman spectroscopy is not a practical sensing technique in the field of engineering because of its complexity. In the buckypaper approach, the fragility and transferring strain to the tubes have been roadblocks to developing a dynamic strain sensor for practical applications. Here, a different approach is to develop a carbon nanotube composite strain sensor to overcome these limitations. This approach has achieved fairly good strain linearity by increasing the strain transfer to the sensor. Moreover, this piezoresistive strain sensor is simple and measures the change of resistance like a conventional strain gage.

In order to test the macro-scale strain sensing characteristics, a film strain sensor was cast and bonded onto a glass fiber beam. CNTs were dispersed in DMF solvent and cured in a Teflon mold in a vacuum oven to fabricate the films [17]. The beam displacement and change of resistance of the sensor on the beam were simultaneously measured to build a strain response model and to find the sensitivity of the sensor. The experimental setup to test the dynamic response of the sensors is shown in Fig. 5. All experiments were done at room temperature. A laser displacement sensor (Keyence, LC-2400 Series) is used to measure the displacement of the cantilever beam.

Fig. 6(a) shows the strain response of a SWNT buckypaper sensor. The strain response of buckypaper shows higher sensitivity in the linear bending range. But it shows saturated strain behavior above 500 micro-strain probably because of slip of the nanotubes due to weak van der Waals interactions at nanotube interfaces. While the sensor is compressed, the individual SWNTs may not slip as much as compared to the tension case. Ideally, the strain in the structure is transferred to the nanotubes in the sensor. But the slipping between nanotube bundles may reduce the strain transferred through the sensor and it may degrade the strain sensitivity of the sensor over time.

Thus, a SWNT based composite material was developed to increase the strain transfer across the nanotubes by means of better interfacial bonding. The polymer PMMA was used as a binding material because it is simple to handle and to mix with SWNT in a dimethyl formamide (DMF) solvent. Fig. 6(b) shows the strain response of composite sensor for different percentages of SWNT in the PMMA. Even though the composite strain sensors have a lower sensitivity than buckypaper, they have a quite linear symmetric strain response in both compression and tension. The polymer bonding to the

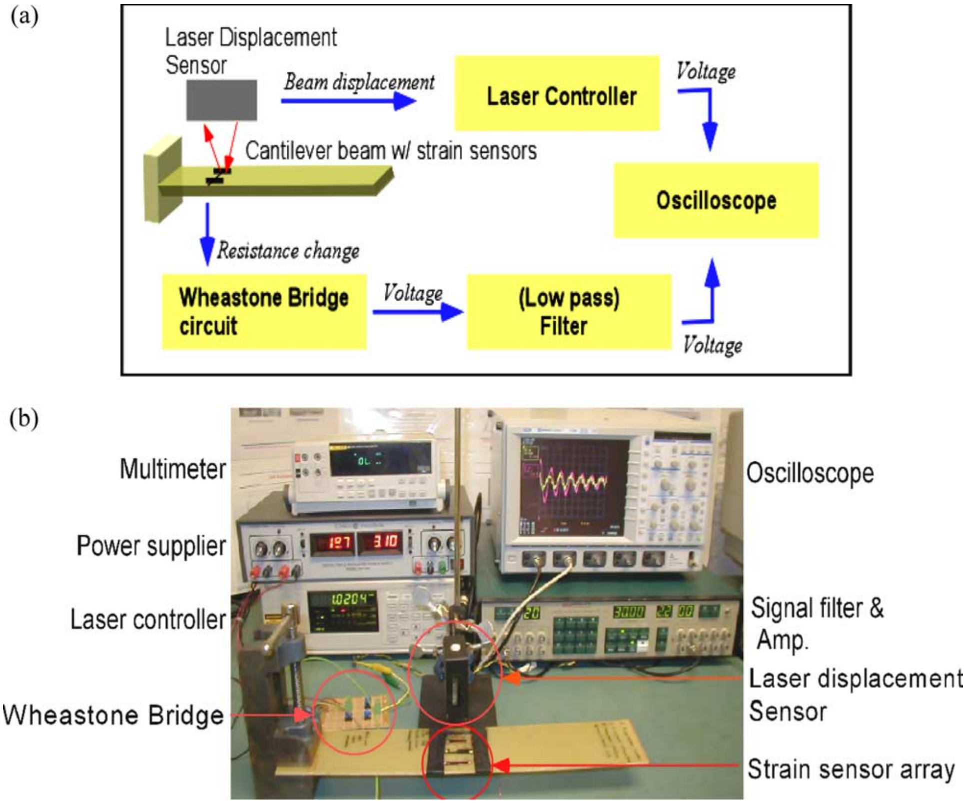


Fig. 5. Experimental setup to test nanotube based strain sensors: (a) schematic; and (b) instrumentation.

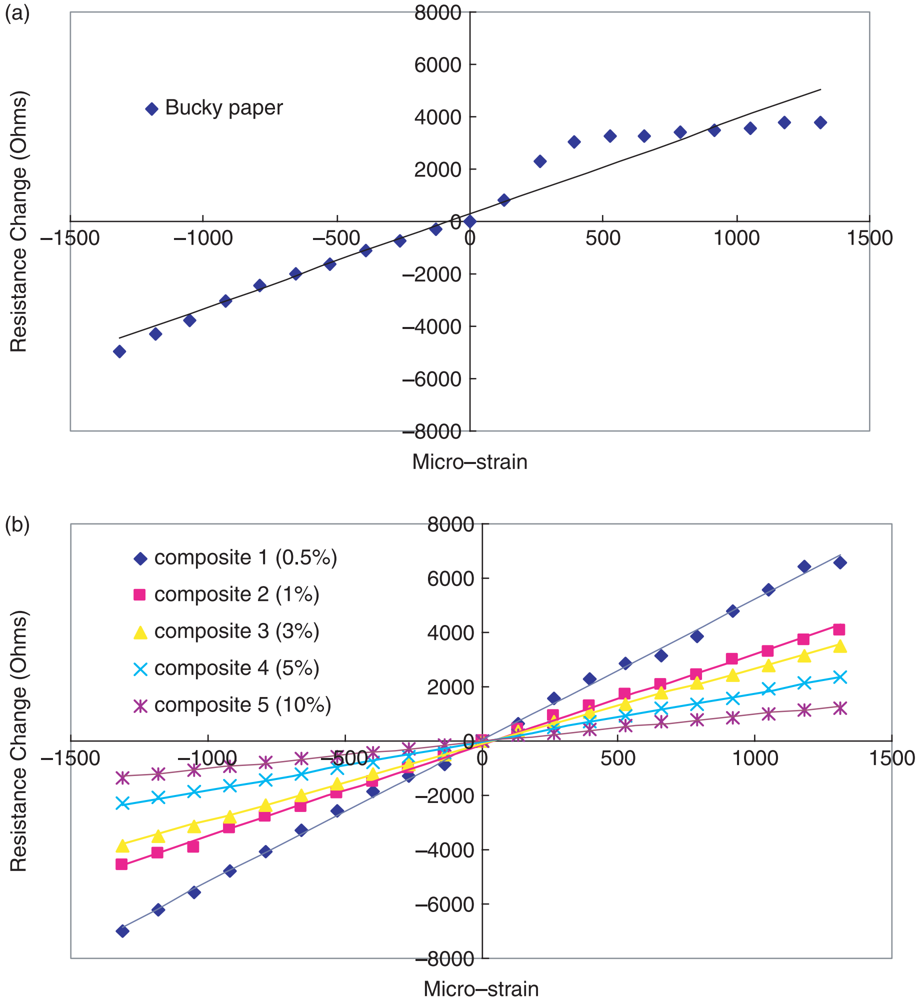


Fig. 6. Strain response of: (a) the buckypaper sensor; and (b) the SWNT/PMMA composite sensors.

nanotubes reduces slip and effectively increases the strain in the sensor.

The sensitivity of the stain sensor is defined as a gage factor (S_g) which relates the resistance change to the axial strain (ε_a) [49]. The normalized change in resistance is related to the gage factor as:

$$\frac{\Delta R}{R} = S_g \varepsilon_a \tag{1}$$

The gage factors of each sensor can be found from this definition and they are the slopes of each curve in Fig. 6. The gage factors of the sensors range from about 1 to 5. The resistivity of the sensor varies from about 0.004 to over 40,000 (cm/s) and is computed based on the resistance and dimension of the samples. The gage factor and resistivity of the sensors show a similar trend based on the percent of SWNT in the composite. Therefore, the strain sensor gage factor and resistance can be designed based on the amount of CNT added to the polymer. It is noted that improved dispersion and processing are still needed to obtain the best performance of the sensor. Good sensitivity was achieved using between 3 and 10 wt% of SWNT in the PMMA polymer.

Fig. 7 shows the dynamic strain response of the strain sensors on the cantilever beam. The beam was set in free vibration by displacing and releasing the end of the beam. The buckypaper strain sensor was tested using a 5 V drive voltage for the wheatstone bridge. The signal was measured using a 30 Hz low-pass filter with 20 db amplification. Above 500 micro-stain the strain response shows distortion at the largest strain level, probably due to slip of the SWNT as described earlier. The buckypaper sensor in Fig. 7(a) thus does not faithfully represent the beam displacement as shown by comparison with the response of the laser displacement sensor. On the other hand, the response of the composite sensor in Fig. 7(b) is almost identically proportional to the output of laser displacement sensor which means the composite sensor transduces the strain signal from structure without distortion.

A structural neuron, which is a long continuous strain sensor, was also developed [17]. The neuron will be used as the sensor element in a biomimetic artificial neural system (ANS) being developed for SHM. The ANS uses multiple neurons to monitor strain and crack propagation in a structure in real time. The CNT neurons can be fabricated as long films on the surfaces of composites [50–52]. A simple method is to build an ANS on a structure using CNT mixed with a binding polymer.

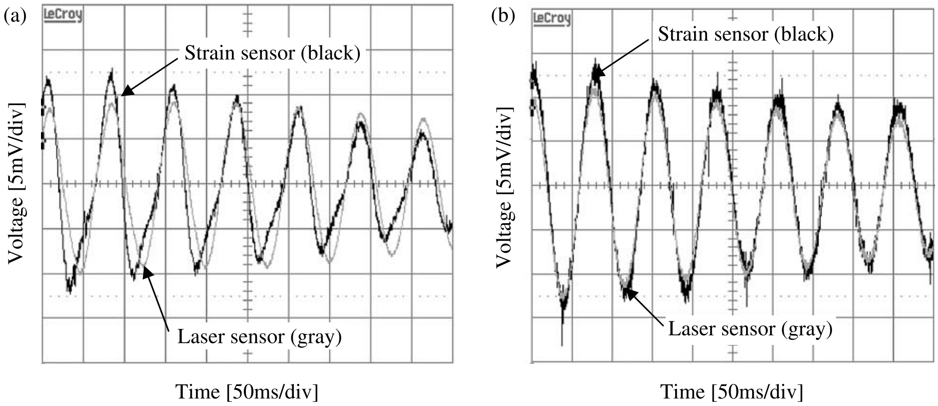


Fig. 7. Dynamic strain response in free vibration (cutoff frequency 30 Hz, gain 20 db): (a) response of the buckypaper strain sensor on the beam; and (b) the response of the SWNT/PMMA 10% strain sensor on the beam.

A mask can be used to define the pattern of the neuron. This method is useful not only for macro-scale structures but also for micro-scale structures such as MEMS. The neurons can be any shape including a grid that is attached onto a structure where the grid functions like the neural system in the human body. By controlling the stiffness of the neuron using different binding polymers, flexible or hard neurons can be built. For instance, the hard neuron is useful for structural strain measurement and the soft neuron is useful for building artificial skin. Because the CNT can simultaneously sense strain, pressure, and temperature, it can be a sensor for tactile systems. In addition, the flexibility of the soft neuron may allow embedding in artificial skin with tactility for an intelligent robot. The high cost would be become a factor for large structures using a SWNT based sensor. Therefore, building an ANS using MWNT or CNF instead SWNT was investigated and can reduce the cost in large scale applications. Fig. 8 shows a MWNT and PMMA 10 wt% composite neuron fabricated on a beam. The strain response is also shown. The MWNT has lower electrical conductivity than the SWNT, and the MWNT neuron shows somewhat less strain sensitivity. The properties of the CNF neuron are being investigated for SHM.

5. Power harvesting using nanotube and nanofiber composites

The potential to use CNTs as actuators has been investigated since 1999. However, using the CNT as a power harvesting system, an interesting related application, has not been studied much. The CNT generates electric energy when it is immersed in a flowing electrolyte. The generation of electric current in CNT when it is immersed in flowing liquids has been theoretically predicted [42] and recently validated experimentally [12]. Kral and Sharpiro [42] reported that metallic CNTs immersed in flowing liquids generate an electrical current because the ions in the liquid have a coulomb drag effect on the free charge carriers in the CNTs. They also noted a direct

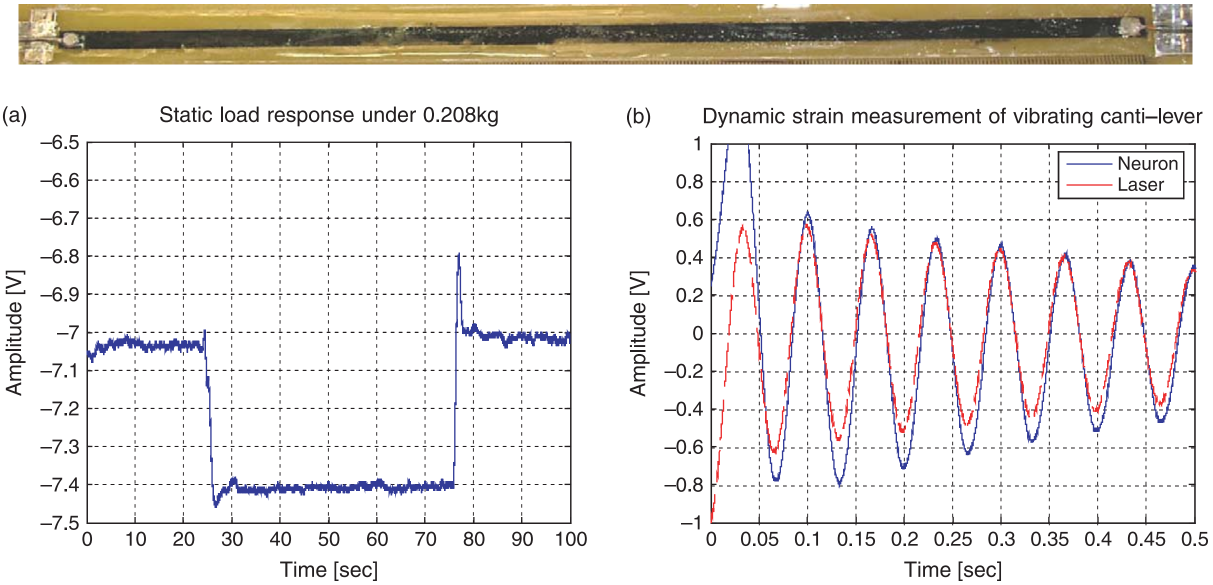


Fig. 8. The MWNT neuron continuous strain sensor and the sensor dynamic response on a cantilever beam: (a) MWNT/PMMA weight 10% neuron (300 mm× 5 mm) on a glass fiber beam; (b) static response under a 2 N tip load; and (c) dynamic repose under free vibration.

scattering of the free carriers from the fluctuating Coulombic fields of the ions or polar molecules in the flowing liquid. Ghosh et al. [12] reported in the experimental observations the magnitude of the voltage/current of CNTs depends on the ionic conductivity and polar nature of the immersing liquid. They developed an empirical equation showing the sensitivity of the generated voltage to the flow velocity.

Power generation in an ionic fluid can have important medical applications such as powering implantable devices. There is also interest in power harvesting for structural health monitoring applications for operating sensors powered from vibrating structures. This power generation and storage for sensing is of great interest for smart structures. Generating and storing parasitic energy with a conversion of mechanical energy into electrical energy using piezoelectric and electromagnetic approaches has been studied and there is limited power available per weight and size of the generator element [53–55]. Thus SWNT and CNF based composite power cells are being investigated for power generation using ionic conductivity for macro-scale applications in engineering. It was found that a bending type motion also produces a voltage signal when the CNT is immersed in an electrolyte [18], an interesting result not reported in the literature. Following this result, a charge generating material was developed for a vibrating structure.

In initial experiments, an induced charge generator was tested in an electrolyte. The voltage measurement is made similar to the strain measurements for the vibrating cantilever beam. Five samples were fabricated; (1) buckypaper, (2) SWNT/sodium dodecylbenzene sulfonate (NaDDBS), (3) SWNT/nafion (95/5 wt%), (4) CNF/NaDDBS, and (5) CNF/nafion (95/5 wt%). These power cells were attached to the beam. Nafion is a solid electrolyte which is a perfluorinatd polymer that contains small proportions of sulfonic or carboxylic ionic functional groups. The NaDDBS is an ionic surfactant, which allows solubilization of CNT in water and dispersion. To obtain the voltage signal from a cell, water was spread over each power cell and the beam was displaced and released to vibrate and cause a relative motion between the nanotubes cast in the polymer material. This relative motion within the electrolyte was expected to generate a charge. The voltage signal was measured with the oscilloscope and a low pass filter and amplifier for easier observation of the signal. The power cells on the glass fiber beam are shown in Fig. 9(a) and the voltage generated by the SWNT based composite generators is shown in Fig. 9(b). The SWNT/NaDDBs power cell had 0.2 mV peak at 12 Hz and it produced 6.5 pW RMS power output. The buckypaper and SWNT/nafion composite also produce a voltage signal due to the beam vibration, but the level is too small to be useful. According to Gosh's model [12], the voltage is a function of the flow velocity in which the CNT is immersed. However, in this case, the binding force of the nafion may restrict the relative motion of the SWNT and liquid and the relative flow velocity becomes small. A CNF based power cell was also developed and its voltage generation is shown in Fig. 9(c). The CNF/NaDDBs power cell had a 0.13 mV peak voltage at 5 Hz and the CNF/nafion power cell had a 0.10 mV peak voltage at 4 Hz.

The impedances of the CNF materials are larger than the SWNT based cell, and their power output is smaller. Having a low binding force, the CNF may not be bonded tightly in the polymer which can allow a small relative velocity between the CNF fibers and the liquid to generate power. Even though the CNF produces lower power, it has a cost advantage and it is possible to build large serial and parallel cells to produce power for SHM. The power generation model is being developed with respect to the dimension of the cell. The effect of ionic conductivity is also being investigated. Increased power generation might be obtained by encapsulating a hydrated layered CNT composite on the surface of a structure and at the same time prevent charge loss through the electrolyte. It is also interesting that the charge produced is flow direction dependent and greater when the flow is in the long direction of the nanotube paper, and this effect will also be studied.

Overall, a power harvesting material has been developed that can be used on a vibrating structure. A solid polymer electrolyte that is hydrated and encapsulated is used to generate charge based on strain of the material and thus eliminate the need for flow of an ionic fluid over the material. The power generated is small, but will be increased, and the material is light and might also be used as a load-bearing material. It is interesting that carbon nanotube composite materials can be formulated for strain sensing (based on piezoresistance), for actuation (based on double layer charge injection and bond expansion), and for power generation (based on coulomb drag), and the transduction effect is different in each case.

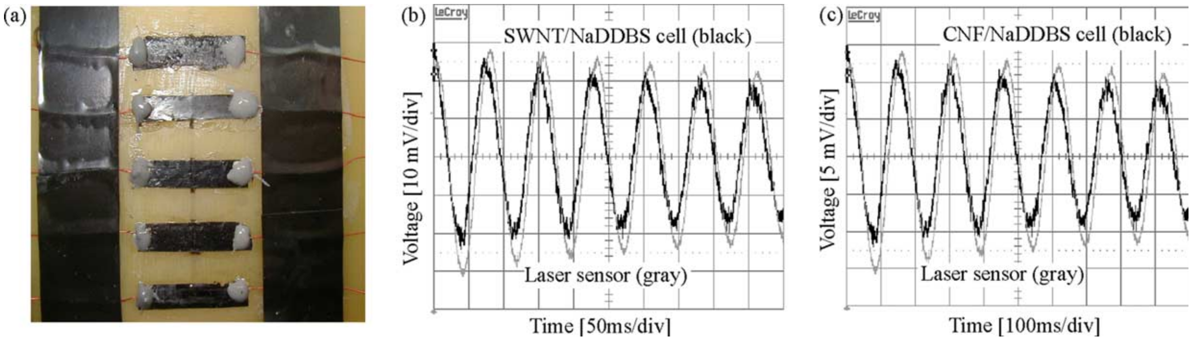


Fig. 9. Power cell and its voltage generating: (a) power cell samples (25 mm×5 mm); (b) SWNT/NaDDBS cell voltage signal; and (c) CNF/NaDDBS cell voltage signal.

6. A carbon nanofiber bioelectronic sensor

Carbon Nanofibers (CNF) are a low cost alternative to MWNT and are used to develop a biosensor based on the electrolytically gated Field Effect (FE) property of nanotubes. Fig. 10(a) shows a sketch of the CNF biosensor. An experiment was conducted for detecting hydrogen peroxide as shown in Fig. 10(b). After tuning the gating voltage, the experiment was run for the conditions of 0.1 V source-drain, and (a) 0.5 V gating voltage, and (b) zero gating voltage. As shown in the upper curve in Fig. 10(c), the current values change sharply with the addition of 2 mM of hydrogen peroxide each time. Actually, the CNF film biosensor possesses a higher sensitivity than the SWCNT film biosensor because the greater conductivity of the SWNT produced a greater leakage current and thus a lower sensitivity to the charge generated by the hydrogen peroxide. The stability of the biosensor is another critical factor for commercial applications. In particular, long-term stability is necessary for biosensor accuracy. The CNF biosensor also produced steady state signals for more than 200 s. On the other hand, without the gating voltage, there was no current increase as shown in the bottom curve of Fig. 10(c). The nearly horizontal line in Fig. 10(c) is when the gating voltage is zero. This result shows the semiconductor behavior of the sensor. This result is for a cm size CNF sensor, which is large for biosensing applications, but easy to fabricate for initial studies. The sensor material using functionalized CNF is shown in Fig. 10(d) prior to testing. As expected, based on the semiconducting property, the CNF biosensor responded effectively to the change in potential of the electrolyte when the gating voltage was appropriately chosen. The biosensor can also be used in an amperometric and Electrochemical Impedance Spectroscopy modes and good results have been obtained for glucose detection using these sensing methods.

The ultimate goal of the biosensor is for detection of disease, and chemical and biological agents (biocides) in the environment. In the context of composite structures, the CNT–FE sensor can be used for chemical detection. This would include moisture, corrosion, environmental contaminants, and material degradation detection. In some applications, the structural material itself could also be a sensor.

7. The potential for intelligent electronic materials

Typical structural materials are electrically conductive such as aluminum, electrically insulating such as polymers with electrically non-conductive fibers, or electrically anisotropic such as polymers with graphite fibers. The electrical conductivity of aluminum is useful to protect the structure from lightening strikes and to shield against electromagnetic interference, and monitoring the electrical conductivity of graphite epoxy composites is useful to detect the breakage of fibers or delamination in composites. Overall, though, the electrical conductivity properties of typical structural materials are difficult to use for smart structures applications, including sensing of damage and actuating the structure.

As described in the previous sections of this paper, CNT/CNF polymer materials are being developed that have electrical and ionic conductivity properties. Essentially, a

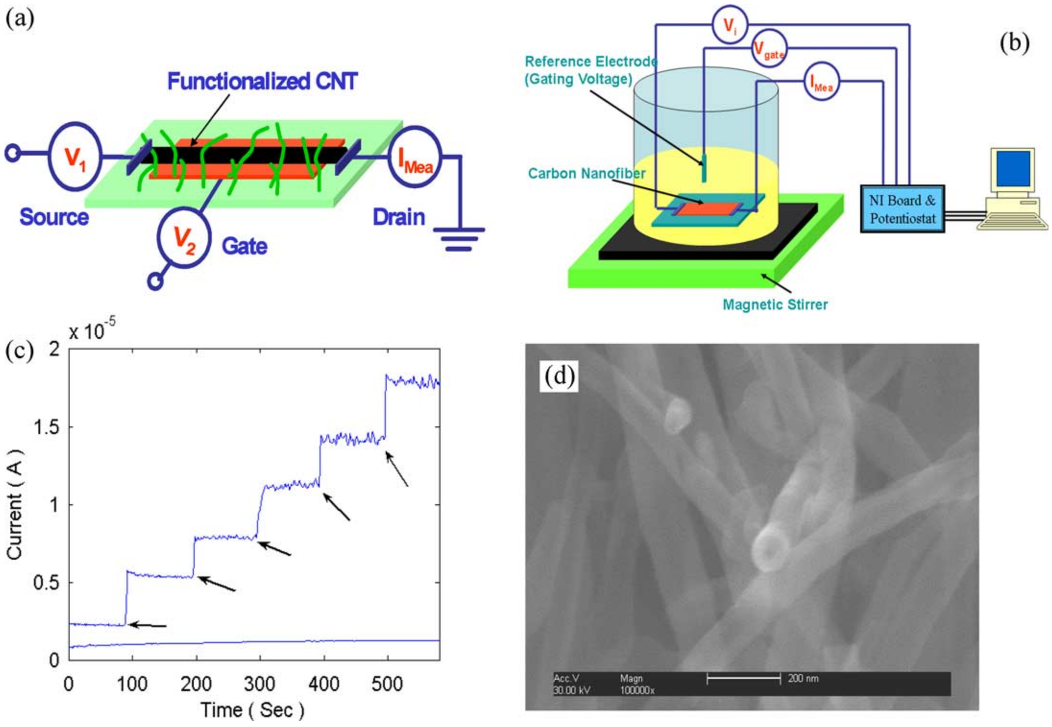


Fig. 10. CNF–FET sensor; (a) transistor design, (b) experimental setup, (c) current response with addition of 2 mM H_2O_2 for −0.5 V (top) and 0.0 V (bottom) gating; (d) functionalized CNF used in the sensor film.

CNT solid polymer electrolyte composite is a semiconducting structural material that can function as a sensor and power generator, as well as an actuator. The sensing property can be based on the electrochemical impedance spectroscopy (EIS) response of the structural material, which has been shown to be highly sensitive to ionic solutions [56], rather than just piezoresistivity. In the literature, proposed techniques for Structural Health Monitoring (SHM) diagnose the structural health by propagating diagnostic waves throughout the structure and interpreting reflections or transmission of the waves that are related to damage in the structure [64]. These approaches have some limitations because they require actuating the structure and using stress wave propagation information to detect small damage or cracks, which becomes difficult in areas of high feature density (joints, stiffeners, changes in geometry). Many piezoelectric ceramic actuator/sensors, wires, and large data storage are needed for this approach.

A new approach to develop smart composite structures is to develop intelligent electronic materials based on a conductive polymer matrix and carbon nanotubes. This material will be lightweight, sufficiently strong, and will sense as well as actuate. The sensing capability allows the material to monitor its own health while the actuation capability allows it to actively improve the performance of the structure and extend its life. In this smart nanocomposite material, EIS can be used to interrogate the structure. This electrical signal is low powered, travels long distances and does not significantly strain the material. The EIS signal can identify changes in ionic and electrical impedance that are related to changes or damage to the structure. In addition, the electronic material can be actuated by applying small voltages over large areas of the structure. The electrical interrogation of the structure may be simpler, faster, less expensive and more accurate than physical interrogation of the structure using stress waves or vibration. The approach of SHM using EIS of the structural material is novel and not reported in the literature, and is under investigation [56,57].

The hurdles that must be overcome to allow nanotubes to be used for the afore-mentioned applications include growing longer nanotubes, controlling the chirality, and properly dispersing and bonding nanotubes to polymers. These are the main roadblocks that are being attacked [48] to bring the great properties of nanotubes to macro-scale applications. Recent advances in growing nanotubes are encouraging. Growing mm long arrays of SWNT using the simple CVD process is reported in [19]. Water injection was used to react with amorphous carbon to prevent the catalyst from being covered and becoming inactive, e.g. $H_2O+C_{am}\rightarrow CO+H_2$. Growing arrays of nanotubes on silicon or steel substrates and removing the nanotubes is a possible approach to allow easier functionalization and alignment of nanotubes in composites, and to allow patterned arrays of nanotubes to be used to form biosensors. Other types of nanotubes including compound nanotubes are possible. Smart materials nanotechnology appears to have enormous potential if the material processing difficulties can be overcome.

8. Summary and concluding remarks

This paper reports the early development of carbon nanotube smart material actuators and sensors that have the potential to improve upon existing smart materials in several areas including increased energy density actuation and sensors with multi-functional electronic properties. It is anticipated that with further development, electrochemical smart materials will allow the actuation of structures, devices, and systems using the structural material itself, which is not possible using any smart material available today. The nanotube continuous strain sensor or neuron discussed is a new approach to monitor strains and crack propagation in large structures such as aircraft, helicopters, and civil infrastructure. The power generation property of carbon nanotubes and nanofibers was demonstrated on a vibrating structure. Lastly, an electrolytically gated carbon nanofiber field effect sensor was developed for biosensing applications.

These results illustrate the continuing development and improvement of nanotube-based materials that is leading to a new class of smart composite materials that can be broadly used in the future with applications ranging from nanomedicine to plastic aircraft. Miniature robots, advanced lightweight airfoil structures with built-in controls, nanotube film wireless motors with high energy density, active biomedical implants, surgical tools, active catheters, and other applications may become practical if processing nanoscale materials continues to improve. In particular, improved nanotube synthesis, characterization, and conductive polymers are needed. New interdisciplinary research ventures, cross-departmental educational programs, and new material characterization facilities are also needed to provide training in the area of nanotechnology to the next generation of students.

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