

# Chapter 9

## CNT Applications in Sensors and Actuators



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### 9.1 Overview

As noted in an earlier chapter, extensive work has been carried out in *sensors and actuators* incorporating or based on CNTs. This includes electrochemically based sensors and biosensors (especially those coupled with DNA and RNA) and other sensor types such as mechanical (e.g., strain) sensors, optical power detectors and acoustic detectors, and fluorescence-based imaging. This also includes “nanomotors.”

### 9.2 Actuators and Nanoscale Devices (Including “Nanomotors”)

CNTs have been studied for such uses as nanoscale artificial muscles [198], nanoscale heat engines [199], and other nanoscale devices [200, 201]. In one study, starting with “aerogel sheets” of MWCNTs, actuators were fabricated that displayed ca. 180% actuation along their width with 5 ms delay time between applying the potential used to activate the actuator and observing the maximum stroke [202, 203], a rate slightly superior to that of the human muscle. However, claims of “artificial muscle stronger than steel and more flexible than rubber” appeared not to be substantiated by the results [202, 203].

Up to about 2010, there was much hype about “*nanomotors*” based on CNTs [204–207] with such phrases as “world’s smallest synthetic rotation motor” [204] and “carbon nanotube electron windmill” [207].

An early (2008) publication from the Wang group at Arizona State University (USA) claimed to show that incorporation of CNTs into the Pt component of asymmetric “metal nanowire motors” leads to dramatically accelerated movement in  $\text{H}_2\text{O}_2$  solutions, with average speeds (50–60  $\mu\text{m/s}$ ) approaching those of natural biomolecular motors [206]. Further acceleration – to 94  $\mu\text{m/s}$ , with some motors moving above 200  $\mu\text{m/s}$  – was claimed to be observed upon adding hydrazine to the peroxide fuel. According to these authors, factors influencing the accelerated movement included the CNT loading and fuel concentration.

However, to date, *there is no CNT-based nanomotor under further development and certainly none in actual commercial or other uses.*

### 9.3 Chemical Sensing, Including Gas Sensing and Electrochemically Based Sensing

One of the claimed advantages of CNT-based chemical (including gas) sensors is that since the sensor is nanoscale, the quantities of analyte required for sensing are also nanoscale [96, 47, 208–211]. Unfortunately, this has not been borne out by practical results to date, as the accounts below will demonstrate.

Some of the first sensing work carried out with CNTs was for sensing of gases such as  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CO}_2$  at the ppm level; this was primarily based on conductometric or capacitive sensing [212–223]. Sensors for toxic gases, including chemical warfare agent (CWA) simulants, and volatile organic compounds such as nitrotoluene (down to the hundreds of ppb) have been tested [224–227]. In some cases, low detection limits, e.g., 10 ppb for a conductometric  $\text{NO}_2$  gas sensor operating at 165 °C [228], were reported, although the nongeneric nature of the conductometric response was not clearly established. Somewhat greater specificity has been obtained in some SWCNT-based sensors. For example, a conductometric sensor using a SWCNT film overlaid with Pd nanoparticles is claimed to be more specific toward  $\text{H}_2$  than other gases [229–231]. Such functionalized CNT sensors have also been demonstrated for  $\text{H}_2\text{S}$  and  $\text{CH}_4$  [232–234].

Microwave resonance has also been used for CNT-based sensing: Naishadham et al. described a unique, highly sensitive antenna-based “smart skin” ammonia gas sensor utilizing CNTs and inkjet printing [235], with the parameter measured being return loss corresponding to change in impedance. Others have also demonstrated microwave resonance-based sensing of  $\text{NH}_3$  using MWCNT and SWCNT sensors [236].

Since CNTs are essentially a carbon allotrope, they can potentially be used for *electrochemically based sensing* wherever carbon-based substrates, such as glassy carbon, activated-C, C-paste, graphite fiber, and other carbon substrates, are used as

electrodes. Potentially enhanced performance is expected due to their nanoscale and higher conductivity. For example, enzymes may be immobilized on them for amperometric detection. A common example is glucose oxidase for glucose detection as used in commercially available, non-CNT glucometers for diabetes patients; in the case of CNTs, glucose oxidase can simply be mixed with MWCNT paste to fabricate the sensing electrode [237]. Examples of such enzyme-based sensing using CNTs abound, including those under test development for, besides glucose, estrogen and progesterone, organophosphates (simulants for chemical warfare agents, with the enzyme organophosphate hydrolase, OPH), proteins, and troponin [238–241]. Detection of dopamine with CNT-based amperometric as well as voltammetric sensors has been demonstrated [242]. Unique adaptations of enzyme-based electrochemical CNT sensors have included a sensor immobilized with the enzyme uricase (for uric acid detection) wherein the MWCNTs used were first functionalized with tin oxide nanoparticles, with the resulting sensor showing a greatly enhanced response over conventional MWCNT-based sensors [243]; a sensor with horseradish peroxidase and methylene blue immobilized on MWCNTs deposited on a glassy carbon surface, for detection of  $\text{H}_2\text{O}_2$  [244]; and a sensor for glucose oxidase wherein, in place of a standard MWCNT paste, a CuO/MWCNT paste was used for reduced response time (down to 1 s) [245]. Catechol has been detected to a level of 0.01 mM using a sensing electrode fabricated from MWCNTs, tyrosinase, and epoxy resin [246].

Unusual or uncommon CNT-based electrodes tested for sensing have included those with MWCNTs incorporated into 1-octyl-3-methylimidazoline hexafluorophosphate gel, into layers of electropolymerized polyaniline, and into microelectrodes modified with (3-Mercaptopropyl)trimethoxysilane for amperometric detection of auxin in plant root samples [49, 247–249]. Other CNT-based electrochemical sensors studied have included those for the detection of homocysteine, brucine, hydrazine, uric acid, L-ascorbic acid, and carbohydrates [250–254].

A unique adaptation of electrochemical sensing to CNT-based electrodes has been *stripping voltammetry*. In conventional anodic stripping voltammetry, a metal ion such as Pb(II) in aqueous solution is first “plated” onto a thin-film Hg or Bi electrode. The Pb metal is then “stripped out” of the electrode in a reverse voltammetric scan. The “pre-concentration” in the first plating step allows for great sensitivity, with single-ppb detection routine. Such a stripping voltammetry technique has been adapted to CNT electrodes due to their observed, superior sorption properties for a variety of analytes. Frequently, the “plating” step does not even need to be at an active, applied potential – it can be at open circuit. Using such techniques, detection of xanthine, 6-benzylpurine, fluphenazine [57], and 4-nitrophenol has been apparently demonstrated [255–258].

Other CNT-based electrochemical sensors include those demonstrated for dopamine [259, 260] (in addition to the work cited above), ascorbic acid [260, 261], norepinephrine [262], NADH [263–265], and  $\text{H}_2\text{O}_2$  [266, 267]. The advantage of CNT-based sensing electrode over conventional electrodes such as glassy carbon appears to primarily be in the lowering of the voltammetric peak potential. For example, in the Nafion-wrapped CNT on glassy carbon sensing electrode used by

Wang's group [268, 266], the voltammetric peak of hydrogen peroxide is at +0.2 V versus Ag/AgCl, whereas on a bare glassy carbon electrode, no  $\text{H}_2\text{O}_2$  peak is observed up to +1.0 V. The high affinity of Nafion toward CNTs was said to play a part in this [268]. Similarly, at a CNT-paste electrode [32], the  $\text{H}_2\text{O}_2$  peak is observed at +0.3 V versus Ag/AgCl [266].

It has, however, not been clear from all the above-cited prior sensing work whether the observed CNT (conductometric, capacitive, microwave resonance, or other) response is simply a generic response to any adsorbed chemical species and whether different analytes present together can be distinguished in any way from each other. The only exception to this is *voltammetric* sensors, since in that case the voltammetric peaks, if clearly distinct and resolved, inherently afford selectivity. In a rare case of good selectivity in an amperometric sensor, Qi et al. [217] showed that, with a polyethyleneimine coating,  $\text{NO}_2$  could be detected without interference from  $\text{NH}_3$ , while with a Nafion coating,  $\text{NH}_3$  could be detected without interference from  $\text{NO}_2$  [217]; however, the sensor was extremely slow, with a response time in the tens or hundreds of seconds.

Additionally, the robustness and durability of CNT-based sensors, a strong requirement for practical field use, are also in question. And the advantages over established sensor technologies have also not been clearly established. A case in point in this regard is the glucose oxidase-based glucometer widely available commercially: Over a dozen different CNT-based glucose oxidase sensors for glucose have been reported, but none has thus far yielded a commercial product, apparently because, for all their advantages, their drawbacks, such as poor robustness, durability, and repeatability, are even greater. Wang's group has attempted to demonstrate that CNT-based electrochemical sensors can be practical by screen printing them in patterns using CNT-based inks, e.g., for the amperometric detection of organophosphate pesticides; however, it was not clear whether these sensors had any greater robustness or stability than conventional CNT-based sensors and whether they also responded to interferents [269, 270].

CNTs have been used for what are known as "*DNA hybridization*" electrochemical biosensors. These immobilize single-strand oligonucleotides onto the electrode surface labeled with an electrochemical indicator to recognize its complementary target [271–274]. Single-strand DNA modified SWCNT electrodes can be used to electrochemically detect the hybridization with target single-strand DNA strands [275]. Such "DNA-CNT" sensors have also been used for other analytes as well. For example, single-strand DNA drop cast onto a SWCNT-FET (field-effect transistor) sensor yielded improved response to methanol, trimethylamine, and organophosphates [276]; and surface-confined MWCNT electrodes subject to absorptive accumulation of guanine nucleobase have been shown to have greatly enhanced response to guanine over comparative non-CNT (e.g., glassy carbon) electrodes [277–279].

Another type of DNA hybridization reported is in a generic type of DNA biosensor [281–287]. In one example of this, amine-terminated probe DNA was immobilized onto the ends of aligned MWCNT arrays using carbodiimide chemistry. The probe DNA had inosine bases substituted for the normally occurring

guanine bases (which are more easily oxidized). The target sequence was labeled with ten guanine bases at one end. Hybridization in the presence of  $\text{Ru}(\text{bpy})_3^{3+}$  allowed highly sensitive detection of DNA, the mechanism being the oxidation of the guanine bases on the target sequence by  $\text{Ru}(\text{bpy})_3^{3+}$  with concomitant reduction to  $\text{Ru}(\text{bpy})_3^{2+}$ . The  $\text{Ru}(\text{bpy})_3^{2+}$  then diffused to the electrode where it was re-oxidized to  $\text{Ru}(\text{bpy})_3^{3+}$ , thus forming a catalytic cycle. The DNA biosensor was estimated to have a detection limit as low as 6 aM (attomoles), much lower than conventional DNA electrochemical biosensors. A DNA probe-doped CP (poly (pyrrole)) film laid over a MWCNT layer was used for AC impedance-based measurements of DNA hybridization [2071]. DNA hybridization has also been detected using differential pulse voltammetry with a DNA-functionalized CNT array that uses daunomycin as a redox label, all intercalated into a double-stranded DNA-CNT assembly [2072].

Tran et al. [288] have described label-free and reagentless electrochemical detection of micro-RNAs using a conducting polymer (CP)–CNT composite “nanoelectrode” wherein the CNTs “interpenetrate” the CP, with specific application to prostate cancer biomarker miR-141. In this work, the electroactivity was believed to emanate from the quinone group in the CP backbone. Response to miR-141, and corresponding lack of response to miR-103 and miR-29b-1, was demonstrated. However, the precise origin of the response to miR-141, and whether other non-RNA interferents would also elicit a response, was not clear.

CNT-based transistors have been used for detection of protein binding, wherein a PEI/PEG (poly(etherimide)/poly(ethylene glycol)) polymer layer is used to avoid nonspecific binding, with attachment of biotin to the layer for specific molecular recognition; biotin–streptavidin binding has been detected using this sensor [289]. A field-effect transistor (FET) has been used for the selective detection of heavy-metal ions, wherein peptide-modified polymers are electrochemically deposited onto SWCNTs and selective detection is achieved by appropriate choice of peptide sequences [290, 291].

Gooding et al. [292] demonstrated protein electrochemistry using aligned SWCNT arrays wherein the enzyme microperoxidase MP-11 was attached to the ends of the SWCNTs aligned normally to the electrode substrate; the practical utility of this for sensing in a real environment was however not apparent from this work. Yu et al. [293] reported electrochemical sensors that used SWCNT forests with multi-label secondary antibody–CNT bioconjugates, for detection of a cancer biomarker in serum and tissue lysates. Greatly amplified sensitivity was attained by using bioconjugates featuring horseradish peroxidase (HRP) labels and secondary antibodies (Ab(2)) linked to CNTs at high HRP/Ab(2) ratio. This approach provided a claimed detection limit of 4 pg/mL for prostate-specific antigen (PSA) in 10  $\mu\text{L}$  of undiluted calf serum. Although this work was published in 2006 and the sensor showed promise, to date no practical sensor appears to have been developed either commercially or in the laboratory.

There has been some work on aptamer-modified CNT-sensing electrodes, along the lines of conventional (e.g., Au) aptamer-modified electrodes; however, this has for the most part yielded inconclusive or negative results [294–297].

CNTs have also been used for what are known as “immunosensors.” For example, Wohlstader et al. [298] reported an immunosensor for the detection of  $\alpha$ -fetoprotein (AFP). Here, antibodies were immobilized on a MWCNT/EVA composite electrode. Capture of AFP resulted in binding of a  $\text{Ru}(\text{bpy})_3^{3+}$ -labeled antibody. Since the  $\text{Ru}(\text{bpy})_3^{3+}$  is chemiluminescent, binding is transduced by the release of light, and the electrode is held at potentials more positive than +1 V. This immunosensor had a detection limit of 0.1 nM and a linear range up to 30 nM. Sanchez et al. [299] demonstrated an immunosensor incorporating CNTs with immunomolecules embedded in a porous polysulfone matrix, with five times the sensitivity toward anti-RIGG than a corresponding graphite-only sensor. The polysulfone embedding afforded good durability to the sensing electrode. Such polymer embedding was also used in other work, for enzymatic detection of human chorionic gonadotropin hormone [300].

An important observation in much work with CNT-based electrochemical sensors has been that electron transfer appears to occur at the ends of CNTs rather than along their walls [280, 301]. For this reason, it has been found that *aligned* CNT arrays yield somewhat sharper voltammetric responses than “random” CNT arrays.

Non-CNT-based amperometric biosensors in which an enzyme such as a dehydrogenase is co-immobilized along with its nicotinamide adenine dinucleotide (NAD<sup>+</sup>) cofactor on various solid electrodes are available commercially for sensing of substrates such as lactate, alcohol, or glucose. The oxidation of the NADH product serves to regenerate the NAD<sup>+</sup> cofactor. Some problems encountered with such systems involve the large overvoltage for NADH oxidation at such electrodes and the fouling of the electrode substrate due to this. It has been shown that such problems can be overcome when the substrate is a CNT-based electrode [268, 302].

Some work has been done with electrochemical sensing wherein the sensor electrode is comprised of a *single* CNT [303, 304]; however, as of this writing, nothing practical has emerged from this work, which thus appears to be of academic interest only.

CNT-based sensors have also been tested for detection of such analytes as hydroxylamine (to 0.12  $\mu\text{M}$  in 3 s) [305]. Detection limits of 50 ppb for chemical warfare agent (CWA) simulants have been claimed for certain SWCNT-based field-effect transistor (FET) sensors and other SWCNT-based sensors [306, 307] although these sensors appear to suffer from problems of irreversibility and/or slow response.

## 9.4 Fluorescence-Based Sensing and Imaging

CNTs have been used for biological imaging [308–310]. Cherukuri et al. [308] used NIR fluorescence microscopy for imaging in phagocytic cells. Welscher et al. [309] demonstrated use of CNT fluorophores for deep-tissue anatomical imaging in mice.

The well-known property of some biological systems to be highly transparent to near-infrared (NIR) light and the strong, intrinsic absorbance of SWCNTs in this NIR spectral window have been attempted to be put to use for optical stimulation of CNTs inside living cells, to arrive at “multifunctional nanotube biological transporters” [311, 312]. In this work, it was claimed that if SWCNTs could be selectively internalized into cancer cells with specific tumor markers, NIR radiation of the nanotubes in vitro could then selectively activate or trigger cell death without harming normal cells. This could be then used to develop SWCNT functionalization schemes with specific ligands for recognizing and targeting tumorous cells.

CNTs labeled with a fluorescent agent have been shown to be easily internalized and then tracked into the cytoplasm or the nucleus of fibroblasts using epifluorescence and confocal microscopy [313].

## 9.5 Other Sensors

Bhandavat et al. [314] recently described a *laser power sensor* based on a composite of CNTs and ceramic material. In this, the ceramic component provides the necessary resistance to high power, while the CNT component provides the very high thermal conductivity necessary to dissipate the heat generated. The sensor could measure powers up to  $15 \text{ kW/cm}^2$  for short ( $<10 \text{ s}$ ) durations of time.

MWCNTs have been tested as tips for *atomic force microscopy (AFM)* and *scanning tunneling microscopy (STM) probes* [314, 315]; however, the claimed advantages (greater flexibility, greater strength) over more conventional tips were not clearly established. An adaptation of this probe or sensing application is the use of double CNT tips as “nanoscopic tweezers” [317].

*Quartz crystal microbalance (QCM)-based piezoelectric CNT sensors* have been studied for alcohol detection [318]. *Surface acoustic wave (SAW)-based CNT sensors* have been studied for detection of a variety of volatile organic compounds (VOCs) [319]. *Thermoelectric-based sensors* have been studied for detection of inert gases such as He and  $\text{N}_2$  and other gases such as  $\text{H}_2$  [320]. *Gas-ionization-based CNT sensors* have also been studied for sensing of mixtures of various gases [321]. These are based on the electrical breakdown of the gases at CNT tips, as the sharp tips of CNTs generate high electric fields at relatively low voltage, lowering breakdown voltages and allowing operation of such sensors at very low power.

A SWCNT film-based strain sensor was reported by Dharap et al. [322]. A linear change in voltage at a CNT electrode was observed upon tensile and compressive stresses. However, since many other materials (i.e., other than CNTs) would also show a linear change in voltage when subjected to tensile and compressive stresses, it was not clear why CNTs were better.

CNTs have also been studied for use as “nano-electro-mechanical sensors” [323, 238] and in *photoacoustic* imaging [324].

## 9.6 Problems and Exercises

1. Give at least two examples of the use of CNTs in actuators, including one on a nm-scale.
2. Describe at least two types of chemical sensors based on CNTs, including details on their principle of detection. Include method of functioning, typical analytes, and typical detection limits and times.
3. Describe at least two types of gas sensors based on CNTs, including details on their principle of detection. Include method of functioning, typical analytes, and typical detection limits and times. These should be different from your answers to Problem 2.
4. What are the advantages and disadvantages of a glucose oxidase-based glucose sensor that uses CNTs as opposed to others that do not use CNTs? Phrase your answer in terms of performance characteristics.
5. List at least five (5) analytes that have been the target of CNT-based sensors. Ensure that you select at least one from the following categories: gases, biologically important chemicals, toxic chemicals, or pollutants. Include method of functioning and typical detection limits and times.
6. Describe the principle of working of a CNT-based transistor and list at least one of its sensing applications.
7. Describe at least one CNT-based sensor using the following principles: fluorescence, laser-based, quartz crystal microbalance (QCM), and thermoelectric. Include method of functioning, typical analytes, and typical detection limits and times.