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Chapter 9

Nanosensors and transducers

Nanomaterials, with their extremely small size, accomplish explicit properties, thus greatly extending the materials science in different fields. The Universe works using the same laws as nanotechnology. The industry surrounding sensors technology today is not exceptional; nanosensors have been under research by numerous organisations for more than a decade. In this, various innovative contributions have been made to nanosensors for various applications. Although there are many present difficulties in their mass production, various approaches to their production have been already demonstrated. The day is surely not far away when nanosensors will see wide adoption and commercialisation. Nanosensors, due to their many virtues presented in this chapter, represent an advancement over current-generation technology.

9.1 Introduction to sensors science and technology

The process of detecting and perceiving various physical quantities is known as sensing. In everyday life, we encounter numerous activities in which sensors are used. More formally, the American National Standards Institute (ANSI) defines a sensor as ‘a system [that] provides a useful output in response to a specific measurand, which can be a physical quantity, property, or event which is being measured’ [1]. Here, what is meant by a useful output is an ‘electrical quantity’, which can be an electrical current, voltage, field, etc. A transducer is an electrical device that is utilised to change one type of energy into another. The words sensors and transducers have often been used interchangeably. The term transducer was preferred to sensor by the ANSI standard. However, the ANSI definition has not been widely adopted, and due to this sensor is the most commonly used term currently. It should be noted that the given definition does not define the general physical components of a sensor. In order to be more specific, terms such as sensing element, sensor and sensor systems are frequently used. The human organism itself has sensory organs like eyes, ears, tongue, the nose and skin. Further, electronic,

mechanical, thermal, chemical and optical sensors are used extensively on a regular basis in cars, smartphones, consumer electronics items, energy equipment, home automation, portable healthcare equipment and many other personal gadgets and public systems. Figure 9.1 illustrates a more precise definition of a sensor based on its different physical components [1], several key terms of which are elaborated upon below:

- Sensing element(s): this component is the fundamental material of a sensor that converts one form of energy into another form. The sensor may have more than one type of sensing element. We define such a sensor as a compound sensor.
- Sensor: sensing elements with their physical packaging and external connection (s) constitutes the overall sensor component.
- Sensor system: this component involves a sensor and its associated signal-processing hardware, which can be analogue or digital and integrated in the same package or discrete from the sensor.

Various commercially available sensors include thermal sensors, colour sensors, alcohol sensors, gas sensors, smoke sensors, humidity sensors, touch sensors, infrared (IR) sensors, heartbeat sensors, glucose sensors, proximity sensors, etc. The list is endless. Some typical performance metrics for sensors and transducers are given below [2]:

- Range: the maximum and minimum value range of the parameter over which a sensor functions correctly. For example, a resistance temperature detector (or RTD) for the measurement of temperature has a range of -200°C to 800°C .
- Accuracy: the error in measurement, defined as the deviation of the measured value from the true value. To extend this concept further,

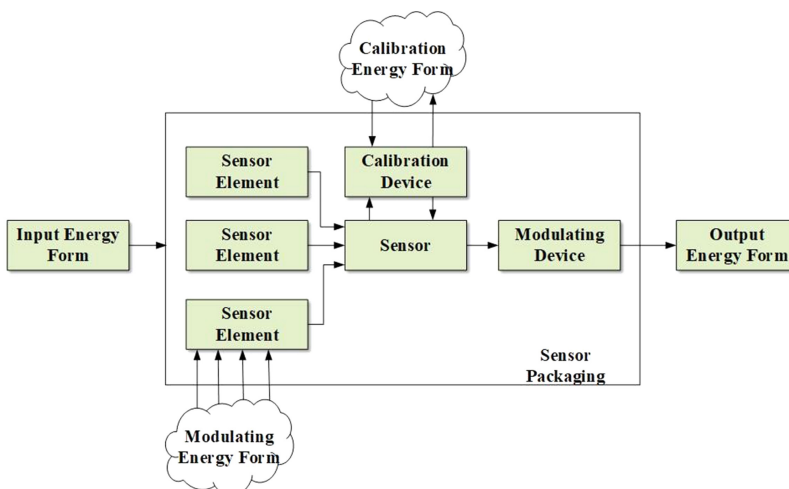


Figure 9.1. Schematic representation of sensor anatomy. Adapted from [1]. © National Academies Press.

absolute error is the measured value minus the true value, while relative error is the absolute value divided by the true value.

- (iii) Precision: the similarity between successive readings while measuring under the same conditions. The values need not be close to the true value. However, when we say that the readings are accurate, it means all the readings are close to the true value and we can further say that the measurement is precise.
- (iv) Sensitivity: the ratio of change in the output parameter to change in the input parameter.
- (v) Resolution: the minimum change in the input parameter that can be detected by the sensor.
- (vi) Linearity: a sensor is expected to behave the same throughout the practical range of the input. This is known as linear behaviour of the sensor. Linearity is the maximum deviation between the measured values of a sensor from an ideal curve, which is a specified straight line.
- (vii) Hysteresis: an increasing or decreasing trend of the input sometimes affects the response of the sensor. Thus, the deviation in the sensor response during different trajectories of the input is termed as hysteresis. Ideally, it should be zero. However, engineers have found ways to utilise the hysteresis property of sensors.
- (viii) Repeatability: the ability of a sensor consistently to produce the same output with the same input and physical and measurement conditions.
- (ix) Response time: the time in which the output reaches a certain percentage of its terminating value.

Current sensor technology faces many issues and challenges. When a sensor interacts with the same environmental conditions, ideally it is supposed to react the same way every time. However, it is often the case that the sensing materials age with time, or are fouled by contaminants in the environment. Generally, current sensor system's response characteristics drift and degrade over time and thus are reduced in accuracy. Future nanosensors may solve this problem by using self-correcting materials or through the ability of the sensors to internally correct calibration drift at the least [3]. Further, as the surface-to-volume ratios for nanoscale materials are much higher than the macroscopic-scale sensors currently in use, their surface reactivity increases, and as a consequence nanosensors will be able to provide better sensitivity. Hence, in situations where the analyte is present in low concentrations, usually large samples are taken for proper measurement [3]. Secondly, integration of various components into sensor systems will be a significant technical challenge because, regardless of the quality, if a sensor is not integrable with the rest of the system, then the system will not perform satisfactorily [3]. It is no exaggeration to say that the field of sensor technology will be revolutionised by incorporating nanotechnology. All the sensor performance metrics, along with the power, performance, area and unit cost of the sensor and the interfacing electronics, can be improved manifold by scaling them to the nanolevel. Nanosensors can identify either tiny particles of an analyte or minimal traces of an external event: they can

detect the presence of chemicals and nanoparticles in a given environment, or physical parameters such as temperature or pressure at the nanoscale. They boast small size, light weight and a huge reactive surface area. Thus, nanosensors are distinguished both by their physical characteristics and their sensing capabilities. Nanosensors find a special range of applications in medical diagnostics, food and water quality assessment, security and biometrics, integrated circuits (ICs), renewable energy sources, display technology, wireless sensor networks, etc [4]. Another advantage, working at the nanoscale, is that various emerging nanostructures such as quantum dots, quantum wires, quantum wells, films, coatings, monolayers, nanowires, porous materials, carbon nanotubes (CNTs), cantilever beams, diaphragms, solar cells, etc. can be used for sensing based on a variety of mechanisms. The response times of nanosensors are very small, making them the preferred tool over other experimental techniques currently in research. In this chapter, we give an overview of some generally popular nanosensors and transducers.

9.2 Nanosensors and transducers in food industry, healthcare and defence

The utility of nanosensors, in a practical sense, does not really have any limit. Including all of them in this book would be an impossible task. As such, we restrict ourselves to some of the most promising domains where consistently positive outcomes have been reported by numerous researchers. It is observed that the food industry, healthcare systems and military equipment in particular are finding the use of nanosensors and transducers to be vital. Typical applications of nanosensors and transducers include identification or detection of various chemicals in gases to detect pollution; medicinal diagnostics, wherein blood-borne sensors or lab-on-a-chip-type devices are used; monitoring physical parameters, such as in the accelerometers used in microelectromechanical (MEMS) devices like airbag sensors; monitoring plant signalling and metabolism to understand plant biology; and in the study of neurotransmitters in the brain to understand neurophysics.

9.2.1 Nanosensors and transducers in the food industry

The most important thing for human life is food. With the globalisation of the food supply chain, food quality and its safety have become primary concerns for human health. Many global food chains supply the same foodstuff worldwide, in which ingredients are procured at their source locations and then distributed around the world to local stores. To this end, many companies sell food that has been packaged. What, therefore, if the ingredients become inedible or unsafe during this process? To address this issue, food quality needs to be checked at all stages of the food supply chain, that is, its production, processing, packaging, marketing and distribution.

Food standards also have been increased following the globalisation of food. So, it is necessary for every food supply chain to check quality at every step of food production. Food safety can be quantitatively evaluated by different techniques, which include fine instrumental investigation and cell culture at the laboratory level. The primary disadvantages of those techniques is their long investigation times,

ranging from few hours to days, ordinarily with various necessary pretreatment steps. These disadvantages, plus other novel difficulties in the food sector, have led to the development of new and fast analytical techniques. In this, nanotechnology incorporated with diagnostic devices presents a crucial solution for the advancement of new gadgets [5]. With the help of nanosensors and nanotechnology, it is possible to check food quality and safety quickly and in an efficient manner compared to biological and chemical methods. Currently, nanosensors are used only in food packaging and transport, and to detect impurities in food; other applications of nanosensors are still at the research level. Nanosensors as used in food analyses combine knowledge from chemistry, biology and nanotechnology, and are referred to as nanobiosensors. In modern life, ordinary sensory exposure to and the ability to check food is prevented by the food packaging, so consumers have to depend on the expiry dates given by the food producer, which are dependent on a set of ideal assumptions about food transportation methods and food storage. But what if these storage or transport conditions are violated before the packaged food reaches the consumer? Clearly, the quality of the food will deteriorate, which the consumer will not discover until the food package is opened or consumed. This disadvantage in food packaging can be solved by nanosensors through their unique electro-optical and chemical properties. Nanosensors can also detect pathogens, chemical contaminants, aromas, gases and even environmental conditions. Use of nanosensors thus ensures that consumers can purchase fresh and delicious food, as well as reducing the risk of food poisoning, which improves overall food safety [5]. To fulfill these tasks, a class of biosensor, referred to as aptasensors (which combine aptamers and nanomaterials) is used. An overview is shown in figure 9.2.

Aptamers are molecules of nucleic acid (DNA or RNA) of approximately 25–40 kDa dimension. Aptamers are target-specific elements, meaning they are highly selective and specific towards their target such as viruses, proteins, microns, toxins, ions, etc. because of their highly tailored structures. DNA aptamers are often robust and can be synthesised with a high grade of reproducibility and purity. They also make biosensor fabrication process easy. In contrast, RNA aptamer-based biosensors, which are easily degraded by endoribonuclease present in biological surroundings, are usually used for one-shot detection. Aptamers can be based on optical, electrochemical and mass transduction label-based or label-free techniques. Nanomaterials are used for signal enhancers or signal transducers. There are many different types of nanomaterials that can be used in aptasensors such as magnetic nanoparticles, carbon nanoparticles, semiconductor nanoparticles, metal nanoparticles, etc. The use of aptasensors is dependent on the kind of nanoparticles used to produce them. Aptasensors are classified into electrochemical and optical systems based on the detection method [6].

A numbers of nanosensors have been developed for the food industry, either for integration into packaging as a nanoscale tracer to show the history of food production or to recognise risks and their tolerance in the event of alleged food poisoning at any time. For instance, nanosensors in food packaging can be made to change colour when certain microorganisms grow beyond a threshold value. This can be used to track storage conditions to prevent food poisoning. In order to detect

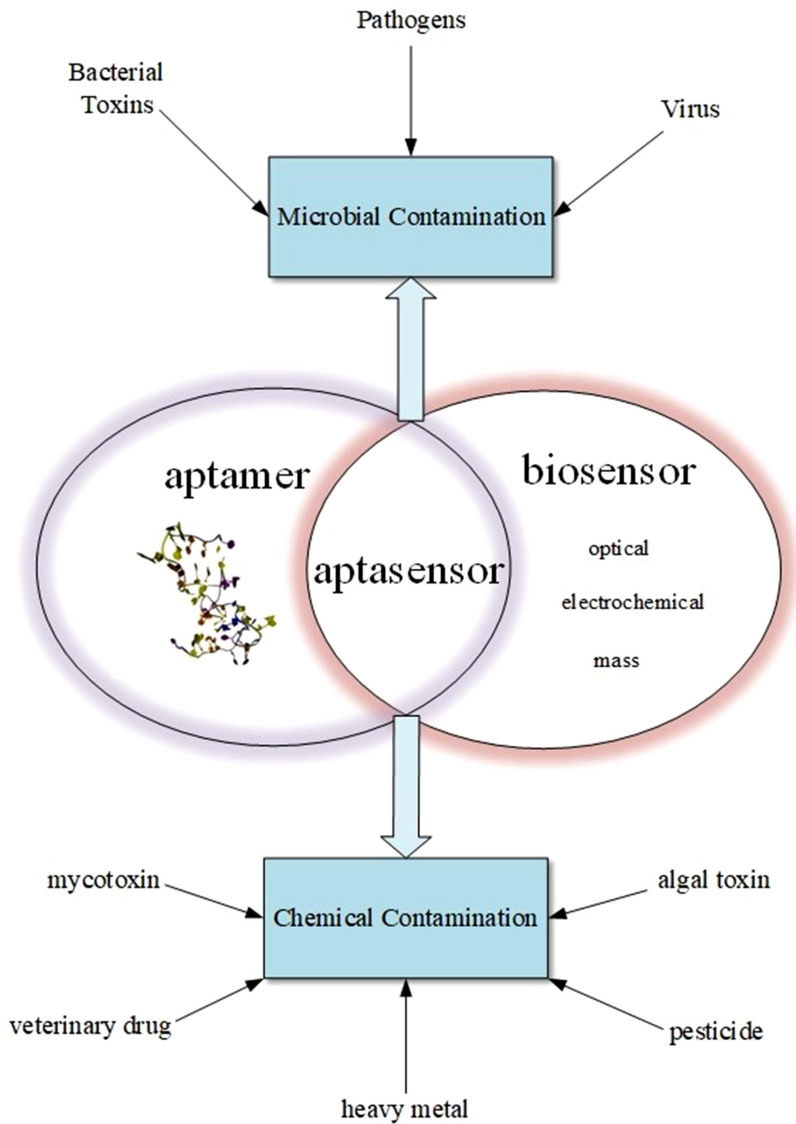


Figure 9.2. Overview of aptasensors.

chemicals like pesticides, gold nanoparticles with appropriate binder coatings can be used. In addition, nanosensors using Raman spectroscopy are ideal for food forensics, wherein a food's origin, contamination and adulteration are investigated. This highlights the unique strengths of nanosensor applications and methods, which enable various analyses of macrofood, preservatives, pigments, carbohydrates, proteins, dyes, etc. Nanosensors can provide quality assurance by detecting toxins, contamination and microorganisms throughout the food-processing chain, using data capture for automated control functions and

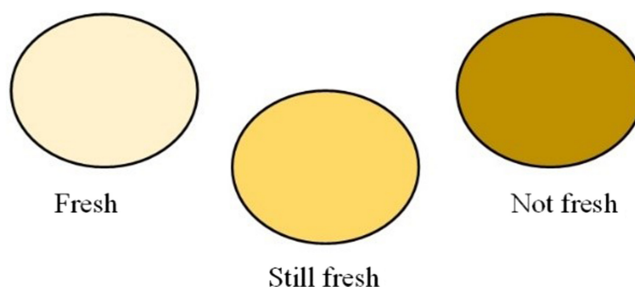


Figure 9.3. Example of a change in the colour of nanosensors in response to food spoilage.

documentation, among other uses; further, nanosensors to detect aqueous toxins are quite close to commercialisation [5].

As mentioned, nanosensors can communicate with food and its environment inside packaging and give an indication of the status of the food. They can respond to changes in the humidity, temperature and level of oxygen exposure. An illustration of the principle of a nanosensor that changes colour according to environmental changes and the condition of the food is given in figure 9.3 [7].

Oxygen detection in food packages using nano-sized particles such as SnO_2 and TiO_2 and methylene blue (redox dye) has also been developed using highly promising photo-activated indicator ink. As in the previous example, when nanosensors come into contact with oxygen, they can be designed to change colour. This method is also used to detect leaks in packaging after production [5]. Smart sensor technology can be used to monitor grain quality, dairy products, fruits and vegetables in a storage and the sources and extent of spoilage, if any. Nano encapsulated flavour enhancers, nanotubes and nanoparticles can be used as viscosifying agents, and so on. In agriculture, nanosensors can be used to sense soil conditions like pH value, moisture, crop growth, heavy metals, etc., and environmental conditions like temperature and humidity. Nanoparticles can also be used to spray and disperse pesticides and fertilisers in a controlled way.

9.2.2 Nanosensors and transducers in healthcare

The healthcare sphere is probably the most likely to benefit from nanosensors and transducers. The intrinsic complexity of the human body, critical diseases and their sequelae, medical treatments with undesirable side effects, etc., often complicate the course of a patient's healthcare. Often, more research is undertaken to reduce the side effects of a strong medicine than into the medicine itself. As a further issue, the symptoms of certain diseases only manifest after a certain time, by which time the condition of the patient has progressed to a critical stage, making treatment complicated that could have been potentially easier had the disease been discovered earlier. For example, pancreatic cancer is typically only recognised after it has spread to other body parts. The same is true with a hip implant; when it is found to be infected, the only way to deal with it is to replace it. Nanotechnology can contribute to this field immensely as materials and structures behave altogether

differently when it comes to the nanoscale, in that their physical, chemical and biological reactions can differ remarkably in contrast to bulk counterparts. The sensing capacity of nanosensors is so high that they can sense low concentrations of harmful viruses, for instance. Hence, healthcare diagnostics, monitoring and healing in a ‘nano’ way has huge potential to improve outcomes. The potential advantages of nanosensors can be leveraged if they are used and improved upon regularly. The purpose of these nanosensors is to gather information at a nuclear scale before transferring it for inspection. Some of the applications in the medical field are mentioned below.

(a) **pH sensing**

Fluorescent sensors contain at least one binding substrate that absorbs and releases some amount of energy when light is thrown onto it. According to any mismatches in the absorbed light and emitted light, a particular molecule can be sensed. The first nanosensor was a fluorescent sensor that measured pH value, for which polyacrylamide particles were used. The given phenomenon can be explained using the example of a receptor and an analyte, as illustrated in figure 9.4, where a receiver response for an analyte is defined by the change in the detected colour. These nanosensors can also be used for glucose monitoring in the body, by exploiting the use of nanoparticles on the skin [8].

Nanowire field-effect transistor (or NWFET) devices can also be used to detect particular species from liquid solution. The same concept is used in pH sensing (the species here is a H^+ ion) [9]. A p-type silicon nanowire can be modified such that its surface charge density becomes sensitive to the concentration of H^+ ions. Changes in the device conductance can be monitored and calibrated to obtain an accurate, linear pH sensor. The higher the conductance (i.e. the lower the surface charge), the higher the pH value.

(b) **Glucose monitoring**

Diabetes is one of the most prevalent diseases in the world. To aid with this, nanosensors offer a new solution to measure glucose. Nanotubes are one of the potential candidate to build such sensors due to their high surface-area-to-volume ratio. At the nanoscale, characteristics like quantum-mechanical

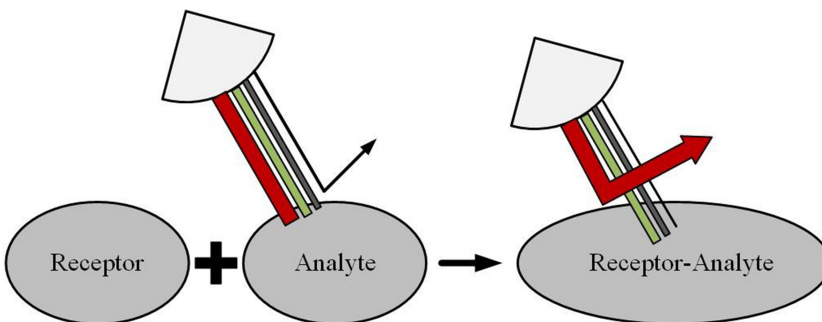


Figure 9.4. Conceptual schematic of luminance dye for intracellular sensing. Adapted from [8]. CC BY 4.0.

changes, optical properties and altered reactivity becomes prominent. The higher surface area improves catalytic activities, which in turn enhances the sensor's sensitivity, signal-to-noise ratio (SNR) and selectivity in measurement. During fabrication, specific substances can be introduced into these nanotubes at high temperature to react with the glucose. The optical properties can change and the fluorescent signal can be measured, which reflects the glucose level. Such sensors are transplanted under the skin and irradiated with a laser. Single-walled nanotubes (SWNTs) that have a large energy band gap absorb greater energy and hence more fluorescence. In addition to this, other options consist of biocompatible polymeric nanosensors implanted under the skin and the use of quantum dots [9].

(c) **Detection of viruses and bacteria**

Although there are several existing methods to detect viruses and bacteria, like immunological assays, polymerase chain reaction (or PCR)-based testing and transmission electron microscopy, they do not show rapid detection if there are few viruses in the sample and they also require some manipulation (or preparation) of the sample. Modified nanowire arrays with influenza A can be used to achieve real-time virus detection. When a virus particle binds to an antibody receptor, the level of conductance changes from a baseline value; when it unbinds, it returns to the baseline value. Using this mechanism, a virus can be detected rapidly [8]. The quick detection of pathogenic bacteria is extremely important in the field of medicine to cure disease. The problem in the detection of bacteria is that existing methods give delayed results and also lack fine sensitivity. Thus, the need for nanosensors arises. Nanoparticles can be easily used to detect molecules such as antibodies due to their high fluorescence. A silicon nitride cantilever can be used to detect *Salmonella* bacteria by the change in surface stress. In the sensing of phage-triggered ion cascade (or SEPTIC) method, a nanowell device with two electrodes is used to identify bacteria through alternations in the electric field [8].

(d) **Asthma detection**

Nanobiosensors can be used to detect asthma attacks. They can detect an attack up to 3 weeks prior by using a hand-held tool to check the level of nitric oxide within the patients' breath. Patients can thus be warned if their levels are too high, or rising. This indicates the possibility of oncoming asthma attacks. A polymer-coated carbon nanotube field-effect transistor (or CNTFET) forms the base of the sensor and contains an arbitrary network of SWNTs between the source and drain [10].

(e) **Astronaut health and safety**

Astronauts spend large periods of time in space and work in space vehicles. Astronauts are also exposed to deadly amounts of potentially dangerous gases. Usually, hydrazine and similar gases are used as fuel by space vehicles. Even at a very low concentrations, these gases are very dangerous. Therefore, the detection and identification of these dangerous gases are very important. To detect these gases in real-time, nanosensors are

used. Any early infection or damage due to radiation to astronauts can be observed by sensing biochemical changes in the body. This can be done using biosensors derived from synthetic polymers called dendrines. Their size is less than 5 nm and are created layer by layer. They are introduced through skin membranes to the white blood cells lymphocytes. The development of this type of sensor can also lead to the removal of the need for blood sampling and testing during space missions [11].

(f) **Nanorobotics in medicine**

Nanorobots can help protect our body from pathogens. A nanorobot is a type of nanodevice with many components such as actuators, controllers, sensors, etc. Surgical nanorobots inserted into the body can act as an on-site surgeon in the body, which are programmed or controlled by a human doctor. They can perform operations like finding pathogens, and diagnosing and conveying messages to the supervising doctor or medical staff through ultrasound signals [12]. Medical nanorobots can be used to monitor cells and microorganisms, for testing and diagnosis in the blood. They have the capability to note and report irregularities in immune system parameters such as pressure and the temperature in various body parts [12]. Nanorobots can also be used in the treatment of genetic diseases. This is done by relating proteins and DNA structure in the cell. The irregularity is thus corrected in the DNA and protein sequence. In place of cell correction, a chromosomal replacement can be efficiently used, which uses in-built repair vessels from the body to maintain genetics. The information stored in the database of a nanocomputer is put outside the nucleus for the purpose of comparison [12]. Nanorobots containing chemical biosensors can be used to measure epithelial cadherin signals' intensity for recognising tumours in their initial stage. They can be also used for drug delivery to obviate the side effects of chemotherapy [12]. Further, nanorobots can help efficiently in addressing dentistry problems. They can be helpful in repairing the tooth, fixing its appearance and in increasing its durability, as well as in oral anaesthesia and treating issues of tooth sensitivity [12].

(g) **Drug discovery and delivery**

The ability to discover drugs in human blood and their pharmaceutical formulation is very important for medical and pharmaceutical science. High selectivity, low sensitivity and minimal interference effects are needed for successful analysis [13]. Biosensors provide many benefits such as real-time analysis, cheap instrumentation, high sensitivity and short analysis time. Biosensors are categorised as a useful signal transduction mechanism and bioreceptor. The different classes of biosensors depending on signal transitions include optical, electrochemical and thermal. The most commonly used transducers for drug analysis are optical transducers and electrochemical transducers. Several biological components like antibodies and enzymes are used in the production of biosensors. The most used components for recognition are antibodies and aptamers, as in drug screening. Up until

recently, several traditional techniques have been used for drug analysis [13]. These techniques offer a good range of detection but have some limitations, as well, such as lengthy analysis times, costly equipment and the need for skilled and experienced staff. Thus, low-cost analytical techniques using biosensors are in high demand, generated by interest in the field of drug science. Compared to traditional techniques, biosensors offer several unique advantages. For the task of drug determination, various biorecognition components and different electrode modification materials are used for the construction of the biosensors. Presently, many biosensor construction methods are being developed to amplify the performance of biosensors. In the years to come, advances in technology may provide low-price, selective and sensitive biosensors for drug analysis [13].

(h) Remote-technology-based nanobiosensors

Technologies for remote sensing are well developed, but applications of these technologies that utilise the noninvasive capabilities of wearable bioinstruments with wireless transmission have just began to appear in recent years. Among these, ring sensors are a very innovative example. A ring sensor is a wearable sensor that is used for observation and monitoring of essential signals. While measuring waveforms for blood volume and saturation of blood oxygen from a finger, it minimises motion artifacts. Ring sensors do not require any kind of slip be placed on the finger of the patient to observe key important signs like pulse rate. A stream of real-time data is fed to the operating system of the sensor to monitor the waveforms. If there is a reasonable amount of deviation in the waveforms, then the ring sensor senses it and can immediately alert a medical professional via mobile or personal digital assistant (or PDA) device by sending a warning [14].

(i) Intelligent Healthcare Data Management Systems

In the past few years, the rate of technological development has been very high. In this general progress, several healthcare-based technologies have been developed based on smartphones, nanosensors, smartwatches and many more. An Intelligent Healthcare Data Management System (IHDMS) is based on nanosensors. It permits a patient or sick person to use healthcare services like diagnostic services, monitoring services and emergency management services from any location and at any time. There are three components to a IHDMS [15]. The first component comprises wearable sensors, worn by the patient. Every nanosensor can identify, represent and process one or more signals, i.e. brain electrical activity monitoring by an electroencephalogram (or EEG) nanosensor, muscle activity observation by an electromyogram (or EMG) nanosensor, heart rate observation by an electrocardiogram (or ECG) nanosensor, blood pressure recording by a blood pressure nanosensor, etc. The second component includes a personal application (or app) that runs on a smartphone. This app accounts for significant commitment. The application is utilised as an interactive interface between the patient's health data, gathered using sensors, and a remote healthcare server to which the patient's

data can be transferred. The third component involves the healthcare server or medical server. This service is accessed via the Internet and is also able to contact other servers such as those of emergency services, healthcare providers and informal caregivers. There is thus a communication channel between the patient's app and the healthcare server. The server collects data from the app and consolidates it into the medical records of the patient. If reports appear to indicate an inconsistent state, the service may allow suggestions or notifications to be pushed to the user [15].

9.2.3 Application of nanosensors and transducers in defence

The present integration of nanosensors and defence into the new realm of 'nanodefence' is expected to deliver advancements in broader areas that will change militaries and play an important role in maintaining national security. There is a belief that nanotechnology can be utilised in two vital ways by military personnel. The first is the scaling down of existing gadgets to enable it to be smaller, lighter, more energy efficient and functionally prompter. The second is to create and adjust new materials for military purposes. Current nanosensing applications in the military use surface coating, nanomaterials and fabrication methods to increase desired capabilities. For example, there are possibilities to detoxify poisonous regions; to detect the beginning of infection in a region presented to military medics; to detect poisons or radioactive material; to secure electronic, data and correspondence systems; to protect human lives and troop safety through the use of nanotextures and related materials; to spy and accumulate intelligence both more accurately and discreetly, etc [16]. In the coming years, nanoscience, nanodesign and nanotechnology will likewise provide lighter, more proficient and increasingly viable military apparatuses; nanorobots for nanoscale devices and frameworks; invisible suits based on metamaterials that are both lighter and tougher; adaptive nanoscale sensors for brain and body sensing; virtual tracking systems for nanoinformation hardware [16]; as well as many other advancements in the defence realm. Some example applications are illustrated below.

(a) Nanomechanical cantilever sensors in defence

Microcantilever sensors have numerous applications in the locating of different analytes in a fluid or vapour. These sensors are characterised by their high affectability, need for minimal stimuli, quick reaction and extraordinary unambiguity. They detect a biochemical response occurring on a surface by approximating a mechanical bending-like event [14].

Explosives such as trinitrotoluene (TNT), dinitrotoluene, pentaerythritol tetranitrate and hexahydro-1,3,5-trinitroazine (RDX) are all substances that pose a threat to public safety. Further, their detection is very hard because they contain a complicated mixture of chemicals, and are revealed only at low air pressures. To address this, by covering a sensor surface with metallic self-assembled monolayers (SAMs), it can detect explosive substances. To detect the particular components of an explosive, cantilever arrays can be utilised. As they feature many reversible receptors, they can detect if any

volatile component is present, even in small quantities. To remove any kind of noise from the environment, instead of using a single cantilever beam an array is set up, as shown in figures 9.5(a) and (b), respectively, which further improves the reliability of the system.

In a second approach, the microcantilever beam's bimetallic effect is used, which probes the IR spectrum of a given substance on the cantilever's surface. It was demonstrated that several nanograms of RDX and TNT on a gold-coated cantilever sensor show a response to 3–5 μm of IR illumination and induce a characteristic bending spectrum, as shown in figure 9.6.

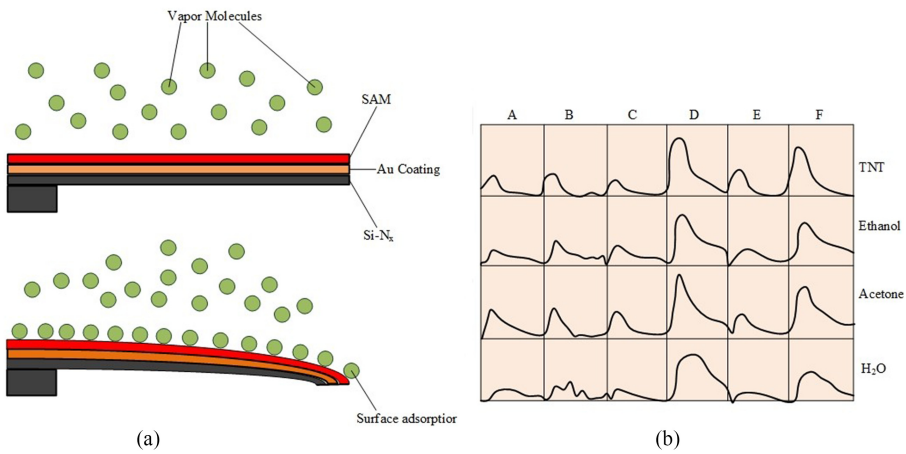


Figure 9.5. Nanomechanical cantilever in explosive detection. (a) A bending-mechanism cantilever sensor, (b) the unique response when an array of six microcantilevers is exposed to water vapour, acetone, ethanol and TNT. [14], adapted by permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>).

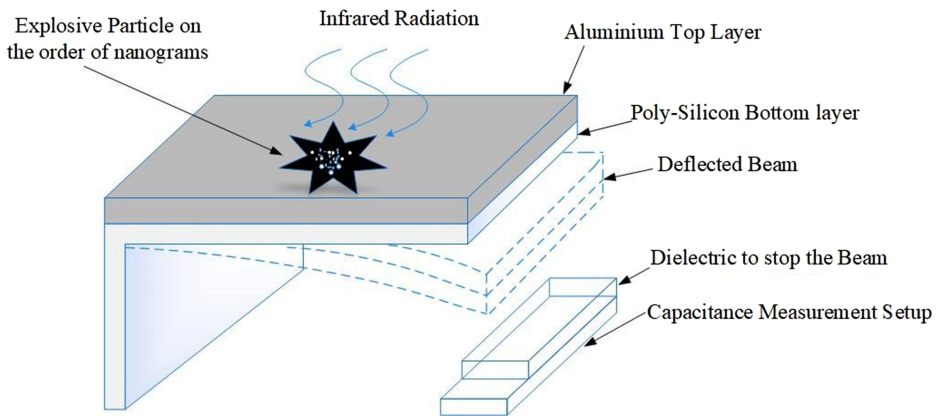


Figure 9.6. Schematic of a microcantilever-based detector to trace explosive particles. [14], adapted by permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>).

(b) Communications in defence

Currently, it is not clear how novel nanosensors will communicate with each other. There are two ways to aid communication at the nanoscale: molecular communication and nanoelectromagnetic communication, as shown in figure 9.7. Molecular communication is referred to as the exchange of information contained in molecular form. Because of their small size and wide operating range, molecular transceivers will be simple to include into nano-devices. These transceivers have the ability to respond to particular molecules and release different molecules in response to internal commands or by following some sort of processing.

The propagation of the released molecules occurs either by active carriers that carry the molecules along predetermined paths, or through spontaneous diffusion of the molecules in a fluid media. However, novel channel models, network topologies, and communication protocols are required by this profoundly altered communication paradigm [17]. By contrast, nanoelectromagnetic communication is characterised as the transmission and gathering of electromagnetic radiation from parts dependent on novel nanomaterials. Ongoing advancements in molecular and carbon devices have opened a pathway to another age of electronic nanocomponents, e.g. nanobatteries, logical hardware and nanomemory at the nanoscale, and even nanoradio wires.

From a communications point of view, certain properties observed in novel nanomaterials will allow them to operate at particular bandwidths and to discharge electromagnetic radiation. Again, however, all these involve an essential change in the present state-of-the-art of logical channel models, network structures and communication protocols [17].

(c) Chemical, biological, radiological and nuclear defence using nanosensors

Today, in the world of technology, weapons development has advanced to an extremely dangerous level. The most dangerous are chemical, biological, nuclear and radiological weapons, which together are abbreviated as CBRN. In the field of CBRN weapons, the ongoing exponential improvement of nanosensors is driving the advancement of efficient instruments for the

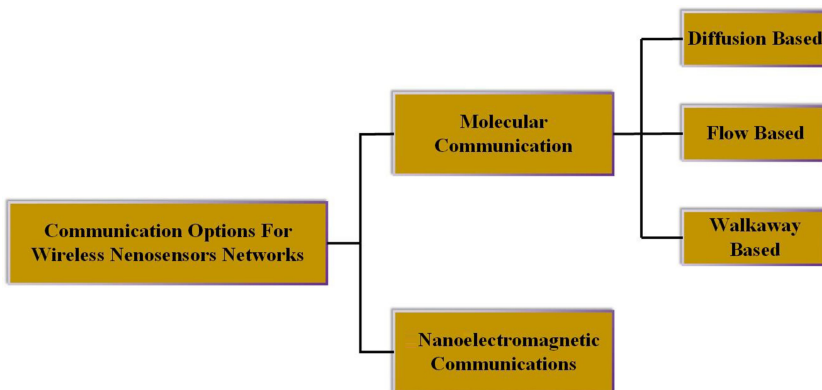


Figure 9.7. Nanoscale communications in defence.

recognition, observation and reduction of CBRN specialists. During the twentieth century, due to the improvement of safety devices, for example activated carbon gas masks, polymer-based securing suits and cleaning arrangements or powders, the potential effects of the use of chemical or biological weapons on the battlefield have been greatly reduced. Nevertheless, with a view towards the future, specific considerations need to be made to assure against new and unconventional weapons. To this end, nanosensors are helping to develop extraordinary strategies, instruments and hardware to neutralise efficiently and successfully the dangers posed by CBRN. In this way, if the pace of advancement in defence technology is high, then the dangers of weapons of mass destruction can be counteracted and the risk to people lessened [18].

Nanoparticles are perfect for heterogeneous catalysis. The uncovered dynamic sites of a solid catalyst must cooperate efficiently with substrate particles and must advance their change. Thus, most heterogeneous catalysts depend on nanoparticles, specifically inorganic oxide nanoparticles as well as metal nanoparticles. Nanosystems with reactant properties would thus be able to assume a significant role in anticipating or limiting the negative impacts on substance, organic and, to a lesser degree, radiological operators. Nano-sized reactant frameworks can find application not just in the location of but also in the security, purification and reduction steps during operations with a hazardous agent. Particularly in the expulsion and destruction of CBRN operators, nanocatalysts have shown great promise [18].

(d) **Military transportation**

Military and guard systems incorporate drones, rockets, shuttle, military vehicles, marine frameworks, ships, satellites and rockets. These frameworks work in the harshest of conditions during battle situations. Interior and outside security systems depend on smart and wise sensor innovation for observation, insight and tactical tasks. In this way, sensors have become a necessary component of military frameworks and in meeting the performance needs of every type of military vehicle, hardware and their related frameworks. Sensors are utilised in in-flight controls, impetus, monitoring the environment, weapon controls, indicators and communications, etc. Today, one can find sensors in various security frameworks, explosives-detection systems, chemical warfare, crime-detection systems, intrusion-recognition systems, and so on. Additionally, sensors are utilised in warzone surveillance systems. These can be deployed on land, in the air, in space and underwater, for concentrated monitoring of a particular zone. Electronic hardware including multiple sensors is a fundamental component of rocket design. With present-day innovation in sensor systems, missiles are considerably more advanced, accurate and powerful as compared to previous generations.

(e) **Futuristic nanosensor applications in military services**

Scientists are gaining confidence in metamaterials to make objects imperceptible. Metamaterials are man-made materials with properties that cannot be found in nature. An optical negative index material (or NIM) can curve light in a manner unlike traditional materials [19]. This can be used to

manufacture an invisibility-cloak-like fabric with seemingly magical properties. Nanotechnology research has aimed to upgrade the characteristics of military attire and its various materials. Future smart uniforms will have nanosensors attached to them, and which will have modified properties to help heal injured soldiers. Further, such technology will make it easier to locate soldiers and to know their condition. Such suits will be able to perform ideal tasks in certain situations. For instance, if a fighter is injured and/or falls unconscious, it might be able to shut itself [19]. As another example, in space elevators the important element in the structure of the airship is the weight-to-power ratio. Making the plane lighter and smaller makes it far less expensive. CNTs show different electrical properties based on the angle or amount of bending, which can be tailored. CNT materials can help to scale down electronics, reduce structural mass and reduce power consumption due to atomically precise materials [19], and thus may lead to better airship weight-to-power ratio.

9.3 Metal nanoparticles and quantum-dots-based sensors

Metal nanoparticles are defined as sub-100 nm entities that are made using metals such as gold, cerium, platinum, zinc, silver, thallium, iron and titanium in their pure form, or in compound forms of hydroxides, oxides, sulphides, phosphates, chlorides and fluorides. Gold and silver metal nanoparticles are examples of single-element metal nanoparticles, with their most common uses being found in medical imagery, while metal oxides are widely used as stabilisers or in paint formulations. The large surface-area-to-volume ratio of nanoparticles make them strong in comparison to bulk materials, and they also exhibit higher surface energies. Nanoparticles have a specific electronic structure owing to the transition between molecular and metallic states, also known as the local density of states (or LDOS) [20]. Plasmon excitation, quantum excitement, short-range ordering, a higher number of kinks and an increased number of low-coordination sites like corners and edges lead them to have very high numbers of dangling bonds and the capability to store extra electrons. A range of metals can be used, but the industry typically prefers using gold metal nanoparticles for a number of reasons. These particles show exceptional properties at the nanoscale, although many applications for them existed years before this discovery. For example, gold is a rare element used in jewellery, coins, medicine as well as electronics. Chemically, gold is considered to be inert as it does not corrode and has a high electrical conductivity. As gold nanoparticles are reduced smaller and smaller in size, they become highly efficient for targeted drug delivery in medicine, and also act as a great catalyst in helping certain chemical reactions. They can also be substituted for iron nanoparticles as they are nontoxic [20]. Further, they can be functionalised easily to develop an affinity towards diseased regions of the body and to help in curing cancer tumours and other such diseases. Their optical properties vary as per their size and are interdependent on their electronic properties. One more special property that gold nanoparticles possess is that they can convert certain wavelengths of light into heat, because of which the free electrons in the

metal can easily move throughout the metal. Thereafter, depending on the size and shape of the gold metal, the gold nanoparticles resonate with the correct wavelength on its surface. Gold nanorods and nanospheres are more efficient in all these functionalities. Gold colloids are widely used to put their optical properties to use in a number of analytical methods, as well as in numerical methods that are used for calculating extinction and scattering across cross sections and other related topics having random shapes as well.

9.3.1 Gold-nanoparticles-based biosensors

Owing to the aforementioned unique properties of gold nanoparticles such as their excellent biocompatibility, strong catalytic properties and high surface-to-volume ratio, they are used extensively in the construction of biosensors. The mechanisms of gold nanoparticles being very efficient, they can be used to improve the analytical performance of sensors. A biosensor based on gold nanoparticles can be designed to interact with an analyte within the body, and the physical/chemical change converted into a signal. Here, the transducing element recognises the analyte and, because of its contact with it, their interaction leads to some physical or chemical change. This change is then represented in the form of a signal [21]. The history of biosensors dates back to 1962. They function using two basic principles: first, the elements that participate in biosensing are actually biological structures; and, second, the sensors measure these biological or physical processes. Gold-nanoparticle-based sensors are highly sensitive in comparison to other conventional biosensors. Essentially, three basic types of biosensor design can be considered: optical biosensors, electrochemical biosensors and piezoelectric biosensors. In these biosensors, different working principles are utilised for the nanoparticles wherein the gold nanoparticles either change their optical properties, electrical characteristics or undergo a change in their mass, respectively.

Optical biosensors are used to measure a change in light output. Surface plasmon resonance (SPR) is the most widely used technique for optical sensing. In SPR, an optical phenomenon takes place because of the interaction between the free conducting electrons and an electromagnetic wave; this is further explained in a later part of this section. A coherent oscillation takes place owing to the electromagnetic radiation, which further excites the electrons present on the surface of the conductor. As a result, a change in the laser light from the surface of the metal film after reflection as a change in the dielectric constant is induced [21].

Figure 9.8 shows a schematic of a SPR detection unit. The SPR signals are amplified by the gold nanoparticles; it has been proved experimentally that the sensitivity of an optical fiber coated with a layer of gold nanoparticles is very high as compared to one without any coating. A number of researchers have devised new techniques to correlate the peak intensity along with the position of the gold nanoparticles' SPR with the surrounding medium's refractive index. This procedure is known as as localised surface plasmon resonance (or LSPR) [21].

Figure 9.9 shows the signal amplification mechanism of gold nanoparticles in a biosensor. The bioreceptors and analytes immobilise the gold nanoparticles. Owing

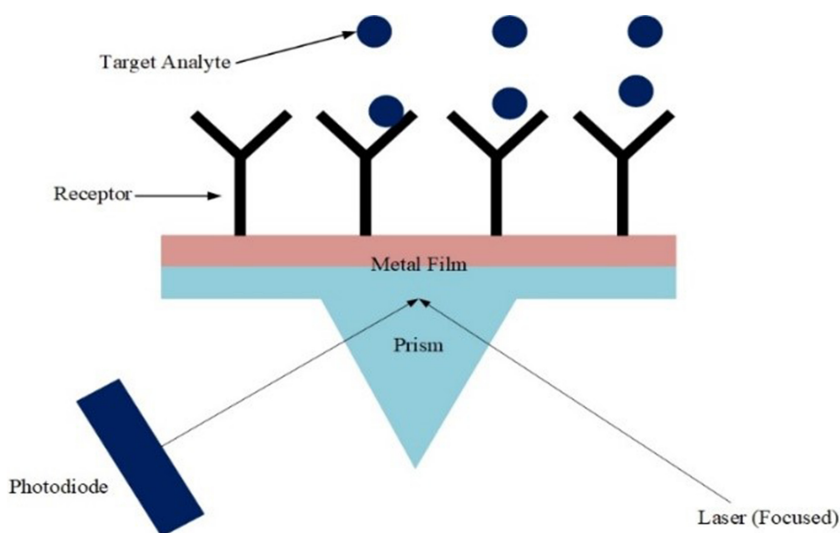


Figure 9.8. Schematic of surface plasmon resonance detection unit. Adapted from [21]. Copyright (2010), with permission from Springer Nature.

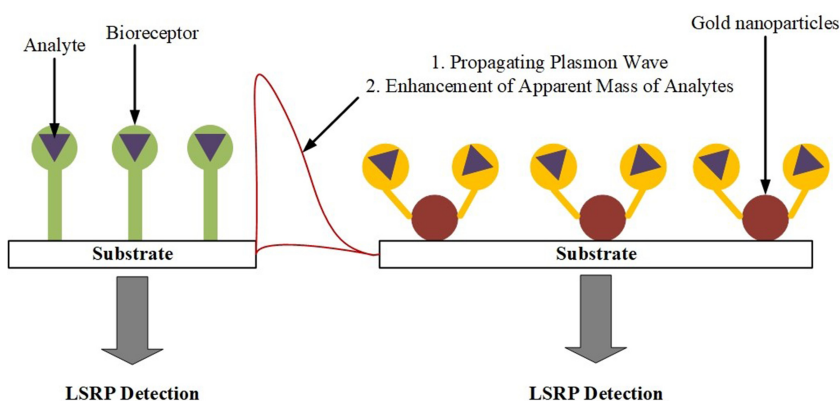


Figure 9.9. Propagating plasmon wave where the gold nanoparticles, bioreceptors and analytes interact with each other. Adapted from [21]. Copyright (2010), with permission from Springer Nature.

to the high density and high molecular weight of these gold particles, the mass of the immobilised analytes on the surface is increased. These sensors can also be structured in the form of arrays to increase throughput screening of the interactions between the biomolecules.

Electrochemical sensors can be used to obtain useful electrical signals by converting the interactions between biological elements; these are referred to as electrochemical biosensors. For this, gold nanoparticles have a number of advantageous properties such as their larger area, better biocompatibility and conductivity; thus, they are widely used to analyse electrochemical signals within the body. Alternatively, materials like quartz, tourmaline, topaz, etc. are said to exhibit a

piezoelectric effect. Piezoelectric biosensors are used to analyse the biological recognition processes taking place and thereafter by measuring changes in mass. A combination of gold nanoparticles with other materials is a key factor in the design of piezoelectric biosensors.

9.3.2 Metal-nanoparticles-based colorimetric sensors

At the nanoscale, gold particle solutions have a specific absorption spectrum and display different colours to their bulk counterparts based on their sizes and interparticle distances. This strategy of detection using gold nanoparticles is effective, easy and fast, and hence it is used in the detection of hazardous chemicals. Gold nanoparticles with particle distributions from 1 nm to 100 nm are referred to as colloidal gold. With alterations in the size of the particle and interparticle separation between the gold nanoparticles, the characteristic peak absorption wavelength shifts from ultraviolet (UV) to the visible spectrum due to SPR.

This mechanism facilitates its use in environmental sensing tasks. Figure 9.10 explains the process whereby gold nanoparticles can be used to detect target matter using its optical properties. Optical sensing technologies based on gold nanoparticles can be deployed by using the integration or disintegration of the gold nanoparticles with the targeted element. This will cause the solution of gold nanoparticles to change its colour from red wine to blue, corresponding to its surface plasmon property discussed earlier. This shifts the absorption spectrum related to this property from 523 nm to 610~670 nm. Optical sensors intensively use this SPR property of gold nanoparticles. It arises when there is vibration among the free electron, giving rise to a certain frequency, which in turn resonates with the frequency of the light that is incident on the solution. This causes the solution to shift the frequency spectrum of the maximum possible wavelength from one spectral

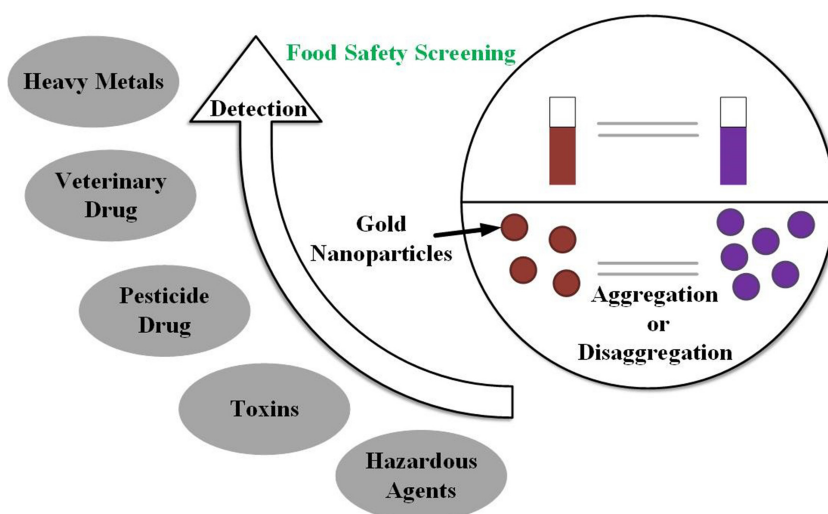


Figure 9.10. Gold nanoparticles responding differently to different wavelengths. Adapted from [22]. CC BY 4.0.

region to another depending upon the frequency that was incident on the solution. This shift is caused due to a change in the size of the particles or by changing interparticle distance between the particles in the solution due to the resonance frequency. Figure 9.11 shows a basic experiment, conducted by Liu *et al* [23], to sense the presence of atrazine using a cysteamine-gold nanoparticle solution. The experiment illustrates that the solution changes its absorption spectra with varying proportions of atrazine.

There are two main determining factors for the colorimetric sensors that determine their response time, sensitivity and SNR [22, 23]. One of these factors helps in determining the specific response or correspondence with the intended substance. The other is the conduction factor, which converts the change in colour to the spectral detection and, hence, simulates the sensitivity effect. This can be used in the detection of toxins from food samples; as aforementioned, the problem of food contamination is one of the major problems faced by supply chains worldwide, and means of early and effective detection are required. In this, different kinds and sizes of pathogens are present in food. Therefore, it is very difficult to detect them in the food samples taken. An atomic absorption spectroscopy technique based on gold nanoparticles, as described above, is very sensitive and selective and hence can be used for this purpose. Fluorescence is the most widely used method for the detection and quantification of biomolecules.

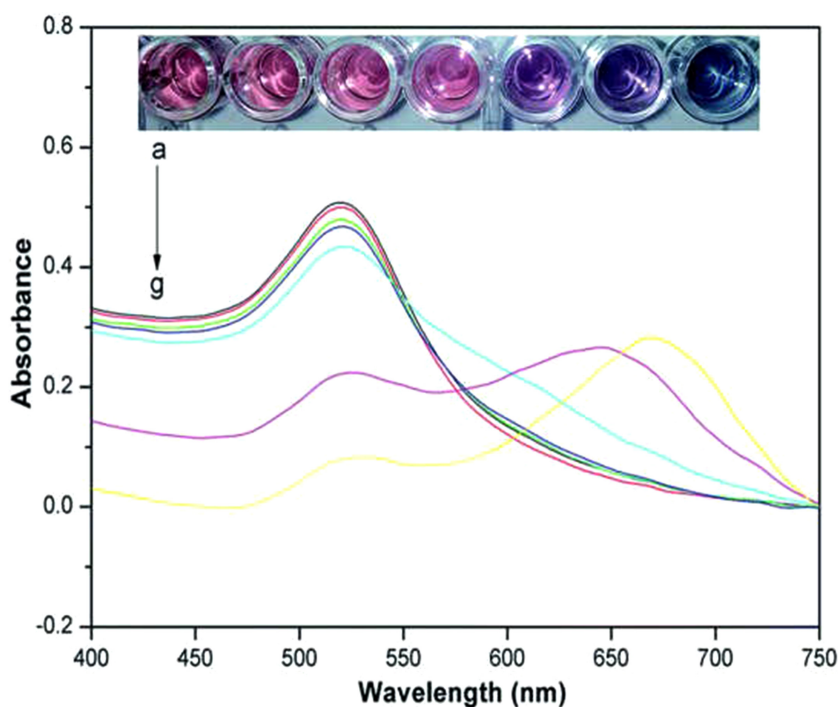


Figure 9.11. The absorbance of cysteamine-gold nanoparticles can be seen to change with atrazine concentration. Reproduced from [23] with permission from the Royal Society of Chemistry.

Nanomaterials, then, offer truly inimitable materials for the development of new methods in chemical and biological sciences. In addition to these, the effects of Raman scattering and ground plasmon resonance can be utilised. With this, rapid steps in the domain of biosensors can be made, and portable instruments based on these biosensors can be constructed. Nevertheless, in view of the versatility of electronic instrumentation for signal conditioning, it is important to concentrate further efforts on electrical sensors. In addition, it should be noted that the use of gold nanoparticles as a chemical and biochemical sensing agent and as a building block for nano-optical devices is not completely understood as of yet. They remain a great area for research.

9.3.3 Quantum-dots-based sensors

Quantum dots have zero dimensions, with high density as compared to the structure of high dimension. For this reason they are widely used in the optical and transport domains. They are suited for sensory applications in the fields of biology, diode lasers and amplifiers. They also play a major role in the detection of ions and small molecules and in indicating pH level. Semiconductor quantum dots have a photoluminescent property, which has an adjustable wavelength. Quantum dots, when illuminated with light, become excited, resulting in energy release as light when the electron falls back to the valence band. The dot sizes can be adjusted to generate different emitted light from identical material, as depicted in figure 9.12.

Quantum dots also possess very high surface-to-volume ratios. As a consequence, they display special electrical properties. Due to these unique optical and electrical properties, they have started to be used in the production of light-emitting diodes (LEDS) and solar cells. Furthermore, these responses to property changes have been utilised to develop sensors. Quantum dots can play a major role in sensors because of their ideal and tunable characteristics. Quantum dots are used in sensors because of their unique properties such as their surficial chemistry, photophysical

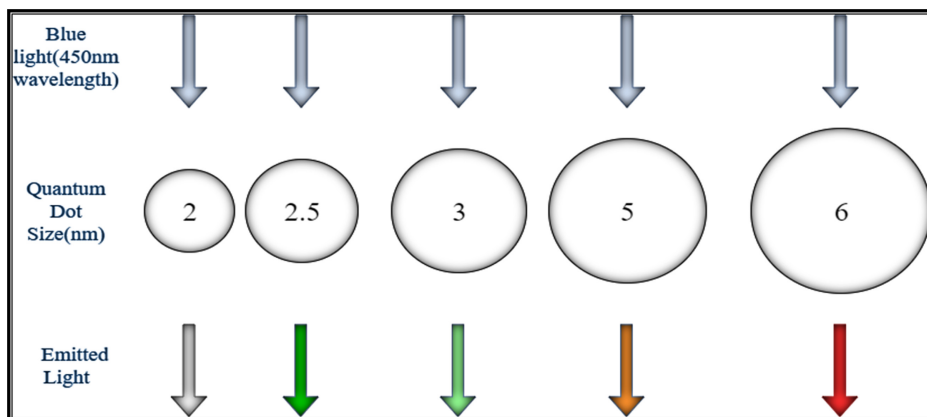


Figure 9.12. Each quantum dot produces a different colour according to its size. Adapted from http://www.nanowerk.com/what_are_quantum_dots.php.

characteristics and binding capacity. They have the capacity to bind with or attach to different molecules while maintaining their fluorescence and photophysical properties. For instance, quantum-dots-based photoluminescence chemosensors have been developed. A quantum-dot chemosensor is a molecular sensor that is used for detecting ions within an analyte by producing a detectable change.

Transition metal ions are used in many processes. However, they pose serious threats to human health due to their toxic properties, and are harmful to the environment. Subsequently, researchers have been trying to develop new methods for their detection. The main principle in the development of these sensors relies upon the functional properties of quantum dots with selective ion reception. There are various methods through which this process can take place. Quantum dots can aggregate due to the removal of receptor on itself; this occurs when the photoluminescence of quantum dots is quenched due to specific collisions among the receptors and ions. Charge transfer can also cause quenching [24]. In the example shown in figure 9.13, cadmium telluride (CdTe) quantum dots and zinc selenide (ZnSe) quantum dots are capped with receptors for the detection of Cu_2^+ analyte. The CdTe is coated with mercaptoacetic acid (or MAA) and glutathione (or GSH), which act as receptors and attract the copper ions. The photoluminescence of the coated quantum dots is selectively quenched when the Cu_2^+ ions bind themselves with the receptors. In this way, quantum dots can also be used for the simultaneous determination of multiple analytes.

Without the receptor capping, quantum dots can still be used for the determination of Cu_2^+ ions. However, apart from Cu_2^+ ions, ions such as Ag_2^+ and Hg_2^+ have shown the capacity of replacing Cd_2^+ . To prevent these competing ions, a coating of thiosulfate is used. The coating of thiosulphate prevents competing ions, making way for Cu_2^+ detection.

Detection of physiological process regulators such as peptides and amino acids can be achieved using quantum-dot sensors. Molecularly imprinted polymers (or MIPs) and attached receptors on quantum dots are the two generally used methods. After the combination of receptor and quantum dot is selected, aspects of the photoluminescence property can be tuned [24]. Nickel is coordinated with dopamine-coated quantum dots and manganese is coordinated with GSH-coated

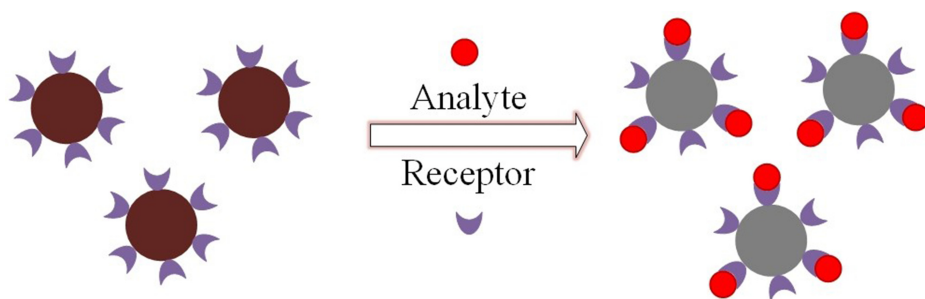


Figure 9.13. Detection of analyte using receptor-coated quantum dots. Adapted from [24] with permission from the Royal Society of Chemistry.

quantum dots. Because of the binding of amino acids and metal ions, recovered photoluminescence is seen. Quantum dots can be covalently linked to MIPs. For instance, GSH, a tripeptide, is overexpressed in cancer cells. Quantum dots can thus be used to build sensitive sensors, thus showing better analysis in cancer studies.

The utilisation of quantum dots for biosensors is yet more interesting due to their optical properties, such as high quantum yields, wide absorption spectra, tight and symmetrically shaped tunable photoluminescence emission spectra, long periods of fluorescence, and outstanding photostability with a solid protection from photobleaching. Indeed, quantum dots have high photostability in comparison to organic fluorescent dyes, and hence they are more suitable for usage in biomedical imaging and related applications. The surfaces/tops of quantum dots can be coated with amphiphilic, hydrophobic and/or hydrophilic types of ligands. These quantum dots can then be linked with proteins, antibodies and/or drugs. As aforementioned, the emission spectrum can be tuned by regulating their size. Quantum dots conjugated with biomolecules can exhibit and 'turn-on' photoluminescence upon interaction with receptors. pH level detection can also be achieved using quantum dots. The process of functionalisation is used in this. This means the process of attaching or interchanging an attached chemical molecule present on the exterior of the quantum dots. Here, the top of a quantum dot can be attached with an organic ligand to impart a sensation of pH. On placing this modified quantum dot in a base, it forms a substance that causes luminance, whereas in an acid it results in a substance that does not absorb in the visible region and is also a poor electron donor. Hence, there is a visible change between the two, which is further a reversible one, making quantum dots a good potential sensor of pH.

In future, quantum dots will surely be very helpful in the domains of research and development. They will play a major role in biological and pharmaceutical research, in the study of tumour detection, stem cells, lymphocytes and embryogenesis. Scientists also believe that, in the future, quantum dots will have a significant contribution to fluorescence spectroscopy. The fluorescent nature of quantum dots may be incorporated into devices. In view of improvements in sensors based on quantum dots' fluorescence, one could move on to reducing the sizes of the same. Scaling in nanoelectronics has been increasing, which could eventually help create a pathway to mobile sensing fluorescent platforms using quantum dots. In summary, there is great capacity for further experiment in the integration of quantum dots on chips with the help of miniaturisation.

9.4 Carbon-nanotubes-based sensors

Because of the high surface-area-to-volume ratio, the sensitivity of CNTs is very high due to their very large contact interfaces in a small volume. As such, even if some target gas is present in a proportion of parts per million, it can be detected. Further properties such as their high tensile strength and high electrical and thermal conductivity can be used to make sensors for specific applications. Also, CNTs are highly sensitive to charge transfer, and so are suitable for making chemical sensors for industrial purposes. CNT-based sensors can be used for various applications

such as monitoring environmental pollution, improving diagnostics in the medical field, chemical detection, quality checking in the food industry, in gas sensors detecting harmful gases in mines, as pressure sensors for medical purposes and in warning systems for military bases.

(a) **Temperature sensors**

Temperature sensors are commonly used in manufacturing industries. CNTs show good electric response with respect to temperature changes, and so considerable sensitivity can be achieved with the help of CNT-based temperature sensors. A spray deposition method is used to deposit CNT films for temperature sensing. For effective sensing, this deposition should be uniform. However, due to van der Waals forces, CNTs stick to each other and so achieving a uniform distribution is difficult. To overcome this, they are dispersed in an aqueous solution of the cellulose derivative sodium carboxymethyl cellulose (CMC). During fabrication, silicon wafers with thermally grown oxides are used as substrates. Photolithography is carried out to define an interdigitated electrodes (or IDE) structure on the samples. The CNTs are deposited by an automated spray system. Before testing, earlier deposited CMC dispersant should be removed, otherwise the CNTs will not be able to touch each other, forming a percolating layer. CMC is removed with the help of HNO₃. CNTs are highly sensitive to oxygen, so they are encapsulated using UV-curable epoxy and glass [25].

(b) **Sensors for pressure and strain measurements**

In the medical field, a microsensor has been designed using SU-8 and polyimide film [26]. SWNT-based resistors are best for this purpose because of their metallic and semiconducting properties as well as compact size. Observations show that this type of microsensor has higher sensitivity compared to conventional piezoresistive sensors. Silicon pressure sensors based on MEMS have a major drawback in that they are not flexible and biocompatible. As such, these types of sensors cannot be used in medical implants. SU-8 is biocompatible and can function in higher thermal conditions. As shown in figure 9.14, two configurations are possible for fabricating pressure and strain sensors, flat-design sensors and cavity-design sensors.

Further, figure 9.15(a) shows the fabrication procedure, and figure 9.15(b) shows a prototype of a fabricated sensor [26]. Figure 9.16 illustrates how

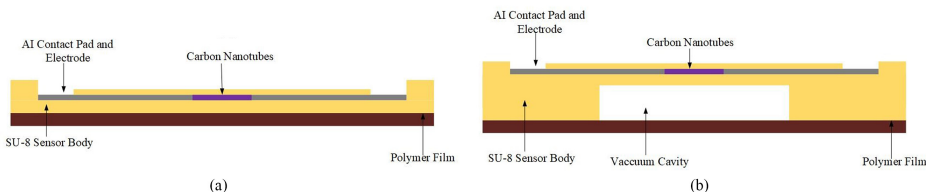


Figure 9.14. Designs of CNT-based thermal sensors. (a) Flat-design sensor prototype, (b) cavity-design sensor prototype. Adapted from [26]. CC BY 4.0.

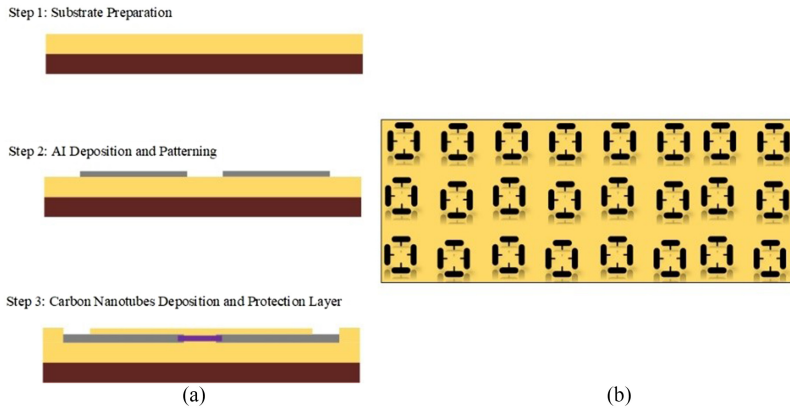


Figure 9.15. Pressure/strain sensors. (a) Process flow, (b) graphical representation of flexible flat-design sensor array. Adapted from [26]. CC BY 4.0.

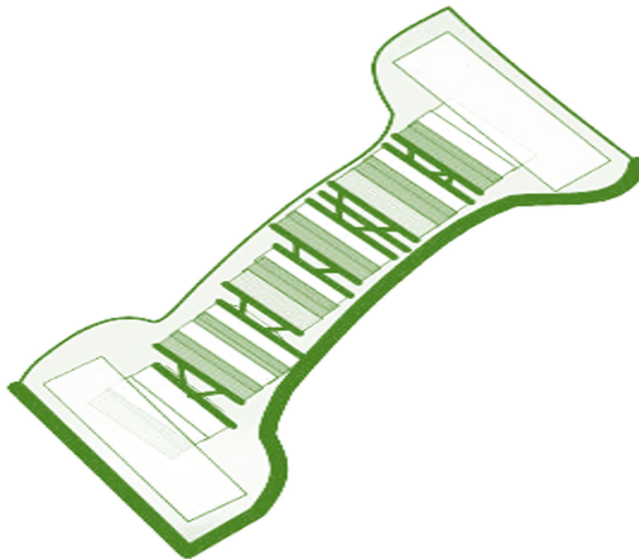


Figure 9.16. Schematic of CNT-based pressure sensor to monitor knee movement. Adapted from [27].

pressure and strain sensors can be used to manufacture a knee belt with which to sense knee pressure in daily life [27].

(c) **Chemiresistive sensors based on CNTs**

One of the most prominent uses of CNT-based chemiresistive sensors is in the form of conducting channels. A demonstration of chemiresistive sensors is shown in figure 9.17. Two main fabrication methods are used to align CNTs between two electrodes. CNT networks are placed between the electrodes with the help of various techniques such as printing, spraying, solid transfer or chemical vapour deposition (or CVD). Conductance

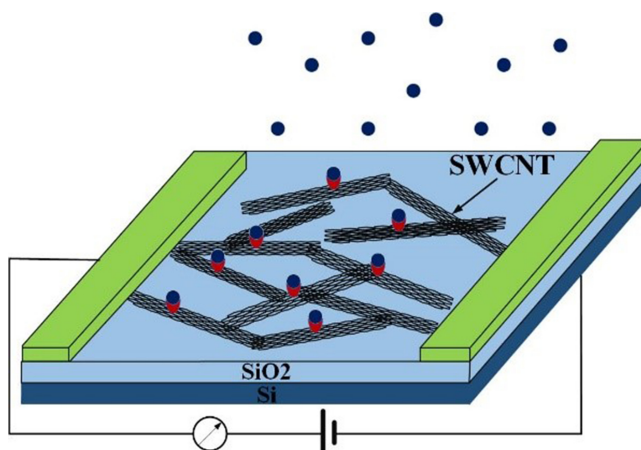


Figure 9.17. Structural configuration of chemiresistive sensors. Adapted from [28]. © IOP Publishing Ltd. All rights reserved.

between the two electrodes can then be measured to check the range and scope of sensitivity. As CNTs mainly consist of surface atoms, a minute change in the chemical configuration of the surrounding environment will result in a change in conductance between the electrodes. The absorption of analytes on the surface of CNTs can result in a change in conductance. For instance, CNTs possess characteristics of p-type semiconductors. As electrons are donated to the valence band, due to the absorption of analytes the number of holes decreases, which will result in a decrease in conductance. Similarly, if electrons are withdrawn from p-type CNTs, the hole concentration will increase, which will increase conductance. The introduction of scattering sites can decrease the charge mobility in CNTs and so the conductance also changes. Further, if the CNT–metal interface absorbs the analytes, then the conductance can also change due to modifications in the Schottky barrier. If an intertube junction absorbs an analyte, then the conductance of CNTs is again modified [28]. Conducting channels are fabricated by the connection of many CNTs, owing to the fact that single CNT units are not long enough to form conducting channels.

(d) **Carbon-nanotubes-based biosensors**

CNTs can be conjugated with several entities, which in turn can potentially enhance their recognition capacity. This also provides a means for them to become multi-functional. Owing to their very high capacity to conduct electricity as compared to that of copper wires, CNTs are beneficial for the transduction of electrical signals generated by the identification of a target. The strength of CNTs is a hundredfold higher as compared to that of steel. Moreover, their thermal conductivity is also much higher than that of diamond. Furthermore, the performance of CNTs in cross-biological membranes makes them very suitable for use in living processes, and that too with minimal invasiveness. CNTs have been shown to be favourable materials to

enhance electron transfer, owing to their electrochemical and electrical properties. This makes them appropriate for fusing with electrochemical biosensors. In order to detect protein biomarkers, metabolites, and so on, diverse electrochemical CNT biosensors have been synthesised [29].

(e) **Gas sensors for detecting the expiration of perishable food**

The main reason behind the degradation of food is the activity of microorganisms, which produce gases like CO_2 . The amount of CO_2 produced is very small, and as such the sensors used to detect the presence of CO_2 need to be highly sensitive. The challenge faced in the synthesis of this type of gas sensor is the high synthesis temperature of CNTs, which is 600°C . This exceeds the maximum permitted temperature of MEMS/CMOS devices, which makes it difficult to integrate CMOS with CNTs on a single chip. To overcome this, a new technique has been developed found in which CNTs are integrated with silicon-based circuits. A microheater consisting of two suspended silicon bridges is used to achieve high temperatures on the chip, as shown in figure 9.18. Thermal annealing is carried out to convert the iron film into nanoparticles at 700°C . The iron nanoparticles work as a catalyst for the CNTs to grow. After this, the CNTs are obtained at 900°C . The thus formed Si–CNT–Si structure acts as a sensor, and also shows the characteristics of a diode with a breakdown voltage of 2.3 V. It should be noted that the detection of CO_2 in an argon environment is relatively simple in comparison to detection in the atmosphere [30].

Power consumption has also been a major hurdle for sensor industries. In this, the development of power-efficient CNT-based sensors has a huge market scope. Miniaturisation is another future goal towards which CNT-based sensors can surely contribute.

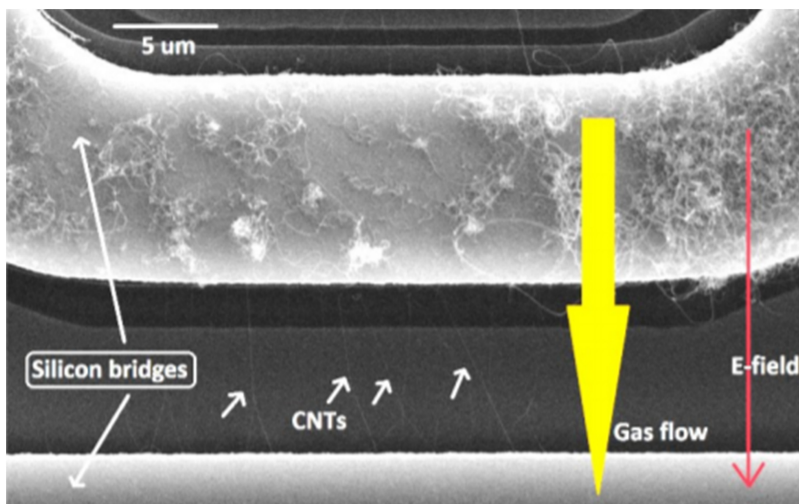


Figure 9.18. Microheater used for the fabrication of CNTs. © 2013 IEEE. Reproduced, with permission, from [30].

9.5 Electronic skin based on nanotechnology

The human skin is the largest organ of the body, with an area of up to 20 square feet. It acts effectively as a very large sensor consisting of nerves. This sensor helps to keep the brain in touch with the outside world by responding to external stimuli. The skin also allows the regulation body temperature with the help of its blood supply, while permitting the sensations of heat, cold and touch. The skin possesses several types of sensory receptors such as free nerve endings, which can detect pain and damage to tissue, and thermal receptors, which can detect a change in temperature. Due to the versatility of the human skin, it is very desirable to imitate its many functionalities in such a way that they can be adapted for applications. Any such 'electronic skin' should be built in such a way that it does not require high temperature or UV rays to be activated. For this, plastic nickel, a conductive metal with the ability to repeatedly self-repair, can be used. The electronic skin can also be sensitive to pressure and highly flexible [25]. Lighting electronic skin is based upon pressure sensors that are fit onto the electronic skin. When pressure is applied to the skin, the sensor's resistance is changed, and with it the electricity flow changes depending on the pressure, hence giving different colours of light. This design consists of a synthetic rubber and plastic composite material, which is thinner than a slice of paper. Organic LEDs are kept between layers and then lit by CNTs and a spot of conductive silver ink. There even is an 'sweating' electronic skin, wherein a soft and flexible device is used that sticks to the skin and can detect changes in the body due to sweat/exercise. This has been developed keeping in mind the possible applications in the field of disease diagnosis. It can also help users to detect how much water (i.e. hydration) is required in the body [25]. Furthermore, in certain areas of medicine, surgeons have to depend extensively on tactile sensation during operations to locate arteries and tissues. This represents a shortcoming for surgical robots as they lack tactile sensation. To overcome this obstacle, the development of electronic skin has proven to be a blessing as it has the potential to provide tactical sensation in order to differentiate between different kinds of tissues. Tactile properties such as elasticity are used to detect unusual stiffness or to discover the positions of tumours. In modern-day health monitoring, the machines used to perform physiological measurements are connected to the patient using wires and cables through complicated wiring, which can cause inconvenience and suffering to patients as well as caretakers. Therefore, it might be beneficial to develop miniaturised versions of these machines that can be attached to the body of the patient directly. As such instruments are attached to the skin of the patient, it would also allow one to collect physiological data from the patient constantly, and might also be helpful in monitoring the effect of a given treatment on the patient. To develop an electronic skin for this purpose, a layer of this skin must have mechanical properties that are similar to those of the human skin in order not to cause any discomfort while wearing it for longer durations. Electronic skin is also useful in the field of smart fabrics. This is an application based on common fabrics and is divided into three categories: sensing, actuating and adapting. Sensing means sensing motion in the environment. Actuating means reacting to sensed objects. Adapting means

being ready to detect, respond and adjust conduct to given conditions. A textile structure can be built up with the help of smart materials by using techniques such as embroidering, knitting, weaving, etc. Sensors give a sensory system the ability to distinguish signals; consequently, in a passive keen material, the presence of sensors is basic. The actuators follow up on the recognised sign either independently or from a focal control unit. Creating mixtures of these source materials can result in an endless scope of novel materials. However, now and then, the business yield is spoken to by pieces of clothing that contain traditional links, scaled-down electronic segments and exceptional connectors. Nowadays, people prefer to wear soft and flexible materials instead of donning rigid structures (i.e. gadgets), so textile materials are the first choice for performing the functions of electronics. Threads can be arranged in such a way (e.g. multiple crossings) to exhibit electrical properties. Also, these properties can be embedded into yarn and a circuit-like element can be made. In this, the core part of the yarn is treated as a gate, as shown in figure 9.19, and the rest can be built up using metals. Such devices are in demand nowadays due to their cheap manufacture, flexibility, large enough surface area for sensing and ease of integration [28].

There are some simple logical insights to the material aspects of electronic skin. A silicon element is used as a substrate for new development. The ability to conform to an uneven surface is an advantage of elastomers in e-skin applications, which also makes it easier to distribute sensors. Specific material properties like tensile strength and biodegradability should also be considered [26]. Polydimethylsiloxane is one of the most important elastomers, which can be used both as a substrate and also as a

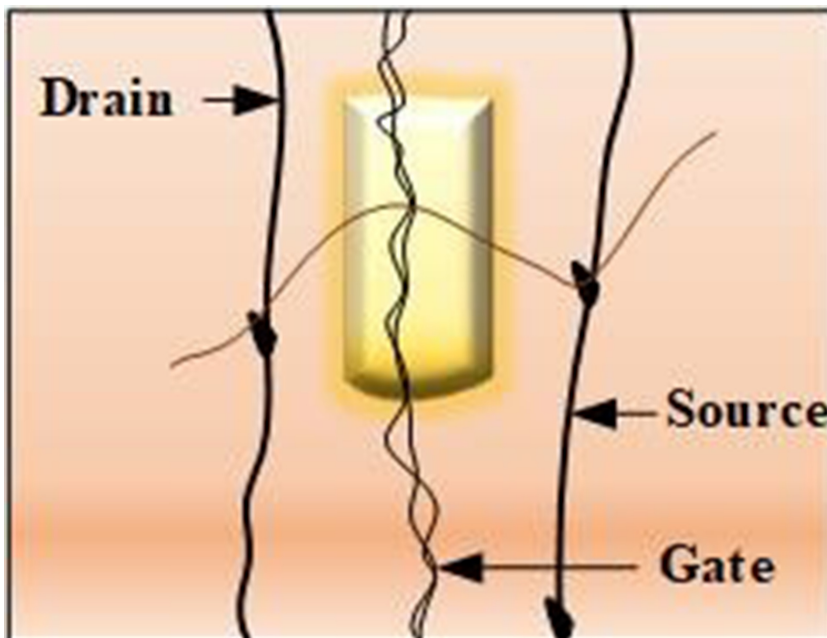


Figure 9.19. Example of building smart textiles. Adapted from [28]. © IOP Publishing Ltd. All rights reserved.

dielectric. It is used to build pressure sensors. The microstructure of this substrate is such that by applying an external force or pressure, it deforms elastically, thus showing its viscoelastic behaviour. Further, its response time is also very fast, so as to be comparable to the response time of real skin. One of the most important components for flexible electronics is a high capacitance for good performance and low-temperature processability [26]. Another likelihood in electronic skin applications is the utilisation of nanowires. Nanowires bring a phenomenal range of possibilities for electronic skin applications, essentially due to their high bearer versatility. Inorganic nanowires are an appealing decision for acknowledging hardware in automated applications. Specifically, semiconducting nanowires have fascinating electrochemical, mechanical, electrochemical and electrical properties, which are ideally suited for various uses, e.g. nanoelectronics, nanotube-based sensors, optoelectronics and photovoltaics [26].

CNTs and graphene are two widely contemplated compounds due to their interesting behaviour. Their intrinsic material properties, for example close to ballistic transport and exceptional mechanical properties, offer another avenue of innovation to improve detection as compared to ultra-slim substrates. In the same way, as with any newly invented material, the effective use of these materials for e-skin and related methodologies depends entirely on the ability to invent reliable fabrication techniques with ease and versatility. Arrangement process procedures, for example turn coating, shower covering and inkjet printing, are only a small portion of the strategies that could help these materials in the advancement of large-scale gadgets. In addition to CNTs, graphene is another contender for the advancement of e-skin parts for mechanical technology and comparable applications. Since the first segregation of graphene, incredible advancements have been made in the amalgamation of its enormous territory. In accordance with these improvements, the coordination of graphene sheets onto ultra-slender, adaptable and delicate substrates could unlock an assortment of applications in mechanical skin, ranging from movement detection to show applications. For instance, the use of graphene sheets of enormous territory as adaptable and straightforward anodes in an automated skin would respect propelled detecting of numerous natural parameters because of their high transporter versatility and high surface inclusion. On the other hand, utilisation of graphene-based adaptable electrochromic gadgets in addition to graphene/nanotube-based keen windows could give skin like showcase boards over the attachments of a human-like device to show data regarding the present status of the framework [26].

Natural semiconductors have helped underlying improvements in the domain of stretchable and adaptable gadgets. Despite the fact that these materials have poor portability in comparison with inorganic semiconductors, the ease of their manufacture and enormous surface regions are some of their relative strong points. Natural materials have colossal planned applications in electronic skin applications. Organic semiconductors are widely used in the improvement of adaptable hardware. Some example natural semiconductors utilised in the improvement of electronic skin incorporate rubrene and pentacene [26]. Polymers, if used as individual components in the domain of flexible electronics, can also help due to their good mechanical

properties, though they also have the drawback of poor conductivity. To overcome this, combining conductive fillers in a polymer can result in a good conductor. Such a combined structure makes a conductive network [26].

Thus, it can be seen that the future scope of electronic skin is based on the capacity of energy storage devices and how reliable the sources of energy are. Material strategies are in research that could lead to the successful integration of the human body with skin-inspired electronics. The inherent limitations to these materials include low stretchability, mechanical stability and areal density, due to which bottom-up approaches will emerge in the near future.

9.6 Microelectromechanical/nanoelectromechanical sensors

MEMS/NEMS sensors have more advanced functionalities because of the addition of mechanical components on the electronic chip, resulting in moving parts being integrated with semiconductor ICs. Typically, integration of the electronic and mechanical functionalities in one single device makes it more compact [31]. Because of their structural properties, MEMS/NEMS are sensitive to a wide range of stimuli such as temperature, pressure, etc. MEMS have countless applications in sensing fields such as airbag accelerometers, gyroscopes, inertial MEMS for automotives, automotive pressure sensors, magnetic field sensors, and so on; as do NEMS devices, being a miniaturised version of MEMS. NEMS have two basic properties: (i) they either deflect or vibrate in response to an applied force, and (ii) they convert mechanical energy to electrical energy and vice versa. These properties allow them to be used as devices by which to measure static or time-varying forces [31]. The biggest future application of MEMS/NEMS technology is in fabricating the smallest possible sensor systems such that they can be applied to nearly any device and used nearly anywhere, in every possible situation. The main goal, then, is to design a device that is able to make full use of the transduction mechanism at these small scales, both at low power and with high sensitivity. Such small-range devices will be able to find use in nearly every man-made mechanism. They also provide high sensitivity because of their structure. NEMS offer even smaller mass and very high surface-to-volume ratio compared to MEMS. Because of this, NEMS are more suitable for applications such as high-frequency resonators or ultra-sensitive sensors. Three of the most widely used types of NEMS sensors are cantilever sensors, graphene nanoelectromechanical (GNEMS) resonators and accelerometers.

9.6.1 Cantilever sensors

Cantilever sensors are used to sense biochemical reactions taking place on their surface by measuring a nanomechanical reaction. There are two basic working principles to such sensors: first, that cantilever bending can be observed due to specific interactions between molecules on the sensor surface and molecules in the analyte; second, that a change in the resonant frequency of the sensor can be observed due to a mass change by molecular adsorption on the surface of the sensor. Two methods exist to measure these changes, optical and piezoresistive, which are described further below. When a periodic function is applied to a system, the

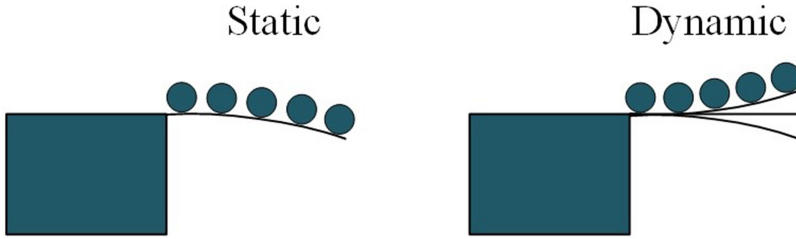


Figure 9.20. The two modes of cantilever sensors, static and dynamic. [14], adapted by permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>).

amplitude varies. The amplitude attains a maximum at a certain frequency, known as the resonant frequency of the system. Much research is ongoing to produce devices using cantilever sensors for biomedical applications. However, the biggest challenge in this aspect is the need for fast functionalisation and reliable output, along with high sensitivity and reproducibility.

As illustrated in figure 9.20, two modes of operation are defined for cantilever sensors [14]. One is a static mode, where bending of the surface is measured; the other is a dynamic mode, where change of the resonant frequency is measured.

(a) **Static mode**

When exposed to the substrate, we can observe some surface stress building up due to interactions on the surface. This stress results in the bending of the surface of the sensor. In static mode, we measure this bending of the surface. Equation (9.1), known as the Stoney equation, shows the relation between stress and the bending of a surface:

$$\Delta z = \frac{3(1 - \nu)L^2}{Et^2} \Delta\sigma, \quad (9.1)$$

where Δz is the cantilever bending amplitude, $\Delta\sigma$ represents the surface stress change, ν is Poisson's ratio, E is Young's Modulus, and L and t are the length and thickness of the cantilever sensor, respectively.

(b) **Dynamic mode**

Mass change can be observed due to adsorption of the molecules of the substrate we seek to detect on the surface of the sensor. Due to this mass change, the resonant frequency of the system changes. In dynamic mode, we measure this change by observing the resonant frequency of the sensor before and after its exposure to the substrate we want to detect by using equation (9.2):

$$f_0 = \frac{1}{2\pi} \sqrt{k/m}, \quad (9.2)$$

where k is the spring constant and m represents the suspended mass. The change in frequency can be calculated by equation (9.3):

$$\Delta f = f - f_0 = -\frac{\Delta m}{2m}f_0. \quad (9.3)$$

Many readout techniques are available, such as optical, piezoresistive/piezoelectric, capacitive, and electron tunnelling, to measure the real-time response of molecular interaction on the surface of the sensor. The most popular are optical readout and piezoresistive readout.

As shown in figure 9.21, in the optical readout technique a laser beam is focused on a surface and the reflected beam is then read by a position-sensitive detector. The deflection in the beam is proportional to the bending of the surface. Hence, the bend can be measured by calculating the deflection angle of the reflected beams before and after performing the experiment.

The most attractive feature of this method is that it can detect deflection in the nanometre range. This method is also very reliable and its setup is quite easy. One of the major disadvantages of this method is that it cannot be used in liquid media as parameters like temperature control, diffraction, etc. are taken into consideration. Further, it is difficult to use this method when using an array of sensors as it requires precise alignment and multiple laser diodes.

Piezoresistive materials have a property wherein their resistivity changes when a strain is applied to them. This can easily be measured by connecting it to an electrical circuit as a resistor. Generally, a Wheatstone bridge circuit, as shown in figure 9.22, is used for this purpose. This constitutes the piezoresistive readout technique.

The main advantage of this method is that the external electrical components can easily be fabricated on the same chip as contains the cantilever sensor, thus making this method more practical to use in the case of sensor arrays. But, when talking

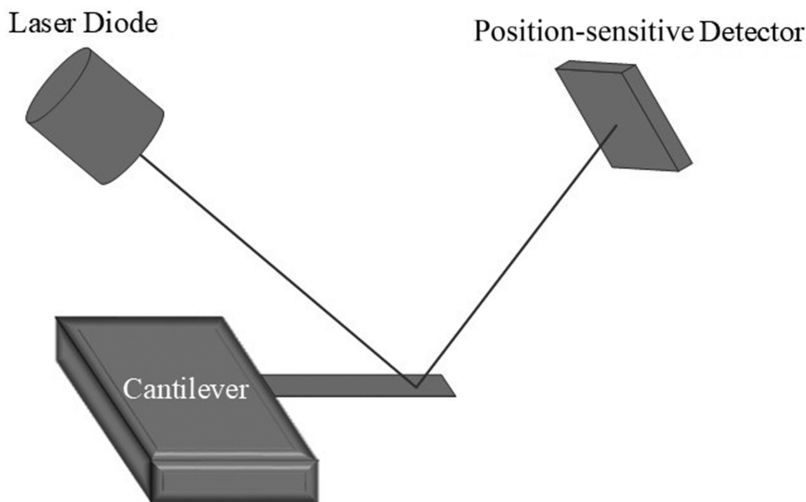


Figure 9.21. Optical readout technique for cantilever sensor. [14], adapted by permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>).

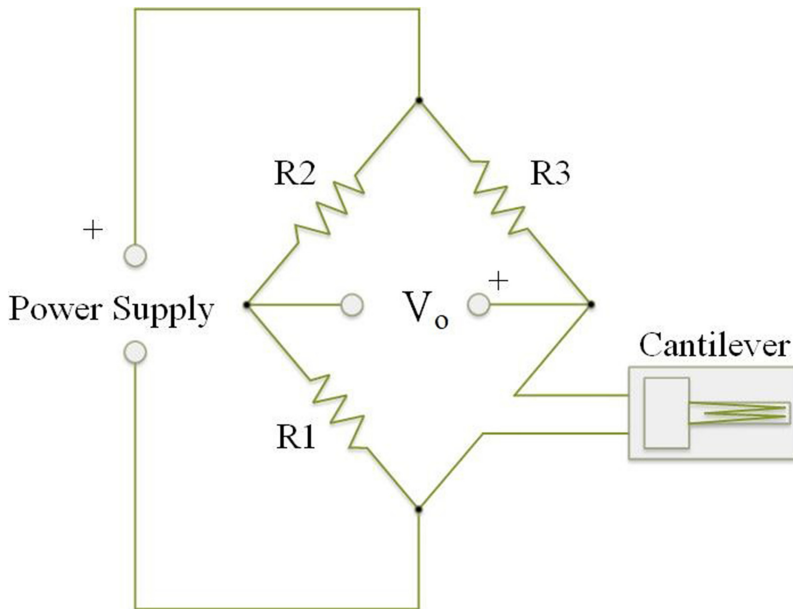


Figure 9.22. Piezoresistive readout technique for cantilever sensors. [14], adapted by permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>).

about electrical circuits, we have to consider built-in noise, which affects the precision of the output by this method. Also, as there is an electrical connection on the chip, there is a need to take extra care while using this method in liquid media. There is also a technological limit to this method, as everything is fabricated on a thin, small chip.

Fritz was first to propose the method of using an array of cantilevers to detect DNA hybridisation [14]. Because of the molecular interaction between DNA molecules and the complementary-oligo-coated surface of a sensor, surface stress can be observed and thus surface bending can be observed. To detect a single mismatch between two DNA molecules, different deflection angles can be measured between sensors coated with different oligo-substrates. Hansen revealed that the deflection angle and beam's direction is dependent on the number of mismatches between the DNA molecules, because as mismatches increase, repulsion forces increase [14]. Meanwhile, research into the application of cantilever sensors in protein identification has been progressing rapidly due to the need to discover disease biomarkers and subsequently to produce healthcare devices that are low cost and easy to use (a disease biomarker is an indicator of the presence of a disease). Moulin observed that different proteins can bend a cantilever surface in different directions and at different angles [14]. In addition, specific antigen–antibody interactions can be observed for disease biomarkers by coating the cantilever surface with a protein-recognition layer. In order to make use of these sensors in the medical field for biomarkers, the sensors should be able to detect protein concentrations and antibody–antigen interactions in a biological environment (i.e. in the blood). To

detect different biochemical molecules, a recognition material needs to be coated on the surface of the cantilever. For example, when coated with phosphoric acid, cantilever sensors can behave as a humidity sensor. The phosphoric acid absorbs water molecules and, due to the mass change, the resonant frequency changes. When coated with gold, mercury can be detected using cantilevers sensors. As mercury is attracted to gold, the resonant frequency changes due to mass change. When detecting large molecules, the dynamic mode of operation is applied as the mass change is greater. One of the most important applications in the detection of gases and vapours that does not require coating on the surface is photoacoustic spectroscopy (or PAS). As shown in figure 9.23, an IR radiation beam is focused through a window. The gas is absorbed by the IR radiation, which in turn produces sound waves. A cantilever microphone senses changes in pressure in the sound waves, and bending can be observed accordingly.

As mentioned earlier when discussing defence applications, there are many explosive substances that are a complicated mixture of chemical compounds which exhibit very low pressure, thus detecting them is a difficult task. To this end, many explosives-detection materials are available such as metals, polymers, etc. that can be coated on cantilever surfaces for the detection of these substances. Cantilever arrays can also be used to detect explosive components in these substances. This method gives very accurate and sensitive readings. Furthermore, as it is not easy to find a substance that is reactive to only one specific explosive substance, by using array setups different coatings can be applied and responses taken from each sensor to determine the exact substance.

9.6.2 Graphene nanoelectromechanical resonators

All sensors, whether developed using top-down or bottom-up techniques, have extremely small structures that are designed to oscillate in response to some mechanical stimuli for their application. In order to sense some particular stimuli, this oscillation is essential. To enable oscillation, these structures require an elastic and inertial element that is situated upon a substrate with appropriate precision.

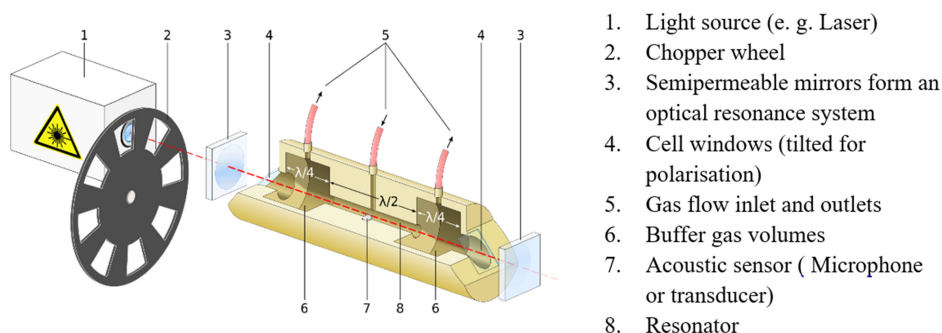


Figure 9.23. Photoacoustic spectroscopy. (This Photoacoustic spectroscopy.svg image has been obtained by the author(s) from the Wikimedia website where it was made available under a CC BY-SA 3.0 licence. It is included within this book on that basis. It is attributed to Hk kng.)

GNEMS resonators are one such structure. To speed up the identification of protein and disease biomarkers, a device that is able to characterise proteomes at the single-cell or single-molecule level is needed. The sensing mechanism of a mechanical mass resonator involves shifts in resonant frequency. Therefore, the basic idea to improve mass sensing resolution is to increase the resonance frequency of the device. With high resonant frequencies, a small fraction of change should also absolutely be large enough to detect easily. The resonance frequency is proportional to $h/L^2 \times \sqrt{E/\rho}$, where h is the thickness, L is the length, E is Young's modulus and ρ is the mass density of the resonator [32, 33]. Based on this, there are two ways to achieve high resonant frequency: (i) by reducing the structural dimension, which makes h/L^2 larger and also the fraction change in mass comparatively large in small-dimensional resonators; and (ii) by using a material with high $\sqrt{E/\rho}$ such as graphene [32]. For NEMS resonators, materials with a high-value quality factor (Q) is used. The quality factor denotes how slowly the oscillation of the oscillator dampens; a high-value Q factor shows a narrow resonance peak in the frequency domain. Thus, a high-value Q factor is desired to optimise the performance of a NEMS resonator acting as a sensor. NEMS resonators have recently been shown to be capable of detecting a mass of 1 dalton. A graphene NEMS resonator can be fabricated using silicon wafers with a silicon dioxide layer on top. After that, graphene layers are suspended from the SiO₂ substrate through van der Waals forces. These graphene sheets are exfoliated mechanically over long narrow ditches that are etched into the silicon dioxide substrate through dry plasma etching. This is shown in figure 9.24. The metallic electrodes can be made through a photolithographic process. They are often made of gold. Vibrations are applied across the graphene layer with fundamental frequencies and detected using a selected readout technique to gain the resonance frequency [33].

Just as in acoustic-wave-based sensors, NEMS resonators are capable of detecting an addition to the mass in a system because of the change in frequency at which the graphene sheets oscillate. The mass of an analyte and its position on the resonator are the main factors that determine these shifts in resonant frequency. As shown in figure 9.25, there is an increase in frequency shift as more and more mass is added.

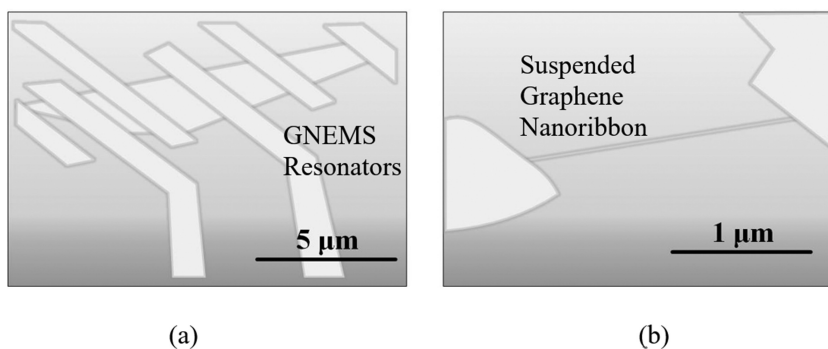


Figure 9.24. Graphical representation of (a) GNEMS resonators, and (b) a suspended graphene nanoribbon. Adapted from [34] with permission.

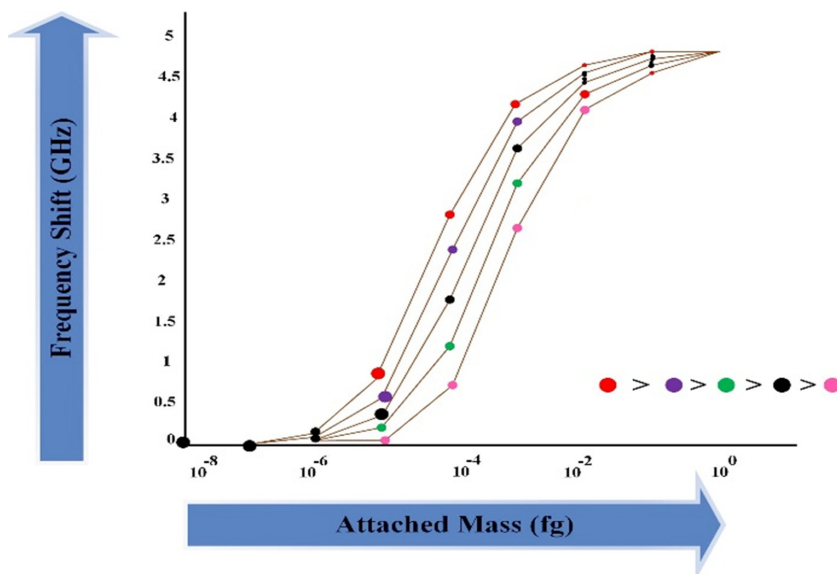


Figure 9.25. Frequency change in accordance with the addition of mass: red dots denote highest mass and pink dots denote lowest mass. Adapted from [33]. Copyright (2013), with permission from Springer Nature.

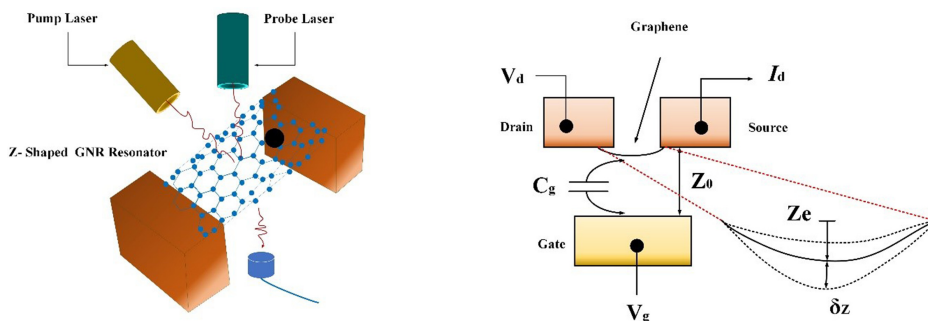


Figure 9.26. Readout techniques for a graphene resonator. (a) Optical, and (b) electrostatic actuation. Adapted from [34] with permission.

There are infinite possible combinations of analyte mass and position for a particular resonant frequency. As such, if the analyte position is known it is easy to detect the added mass.

There are two main techniques to actuate a GNEMS resonator: optical and electrostatic actuation [34]. Figure 9.26 illustrates these readout techniques. In the optical readout technique, a laser is focused on a sheet to modulate it at drive frequency. This modulation results in temperature modulation of the graphene, which causes the periodic shrinking and expansion of a layer. This continuous periodic action results in motion of the sheet. Another laser beam reflects from the suspended graphene as well as passes through it and reflects from the substrate under

it, creating an interference pattern. The intensity of this reflected signal is sensitive to the position of the graphene. Thus, by tracking the intensity modulation of a reflected signal using a fast photodiode, the motion of the graphene can be detected. In the electrostatic readout technique, a graphene sheet is connected to source and drain electrodes, and this structure is situated on a gate electrode. When a DC voltage is applied to the gate, because of the uniform electrostatic force the sheet is statically deflected towards the gate electrode and creates a parabolic shape. By applying an additional radio frequency (RF) signal of frequency W at the gate, resonant motion is created upon the graphene sheet, which leads to RF force. When the RF is applied, the graphene vibrates around its static parabolic shape with a sinusoidal-mode shape. Parts with small deflection (parts near the source and drain electrodes), the difference between exact-mode shape and parabolic shape is infinitesimal and thus ignorable. Therefore, detection of the motion of the graphene using only a midpoint (with maximum deflection) is possible. As this midpoint oscillates, it acts like an actual spring with a static equilibrium position at the midpoint of a parabola. Now, this mechanical motion can be transduced to a time-varying current using graphene's charge-dependent conductance, G . By measuring changes in the current, changes in the resonant frequency can be measured.

9.6.3 Single-chip-based nano-optomechanical accelerometer

Inertial sensors like accelerometers and gyroscopes have applications in the area of maneuver modern vehicles including motorcycles, missiles, aircraft, including unmanned aerial vehicles (UAVs), among many others, and spacecraft, including satellites and landers. The accelerometers used in the past were formed with capacitive, piezoresistive and piezoelectric outputs. Optical sensors have an advantage due to their increased sensitivity. Basically, an accelerometer works by movement of a proof mass with respect to some fixed focal point, by compression or stretching of a piezoelectric material, and then by measuring current. Measuring acceleration with light is a little more complex. Such devices are made of two layers. The first layer contains a proof mass that can move in the vertical direction, as shown in figure 9.27. The second layer on top of it has a hemisphere mirror, as shown in figure 9.28. Together they form a cavity. Most of the light incident on the device is reflected back except the light matching the resonant frequency of the cavity. When there is an acceleration in the device, the cavity changes, and thus the resonant frequency changes. It is then possible to continuously match the intensity to the resonant frequency of the cavity and to calculate the acceleration of the device.

To summarise, in this chapter we have given a glimpse of the fantastic world of nanosensors and transducers. Suffice to say, the contents of this chapter are like a poppy seed as compared to ocean. However, for a student/researcher embarking on the journey of nanoscale sensor design and applications, it will surely pave a solid pathway. A vast literature is available on these and similar topics, and we leave it to the interest of the reader to explore them further. Only one statement can truly express the potential of the world of nanosensors: the sky is the limit. But, again, this is perhaps true of every aspect of nanoelectronics!

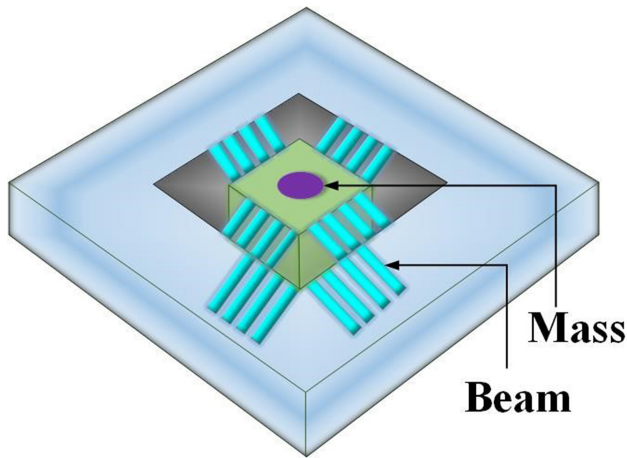


Figure 9.27. First layer of an optomechanical accelerometer. Adapted from [35]. Image stated to be in public domain.

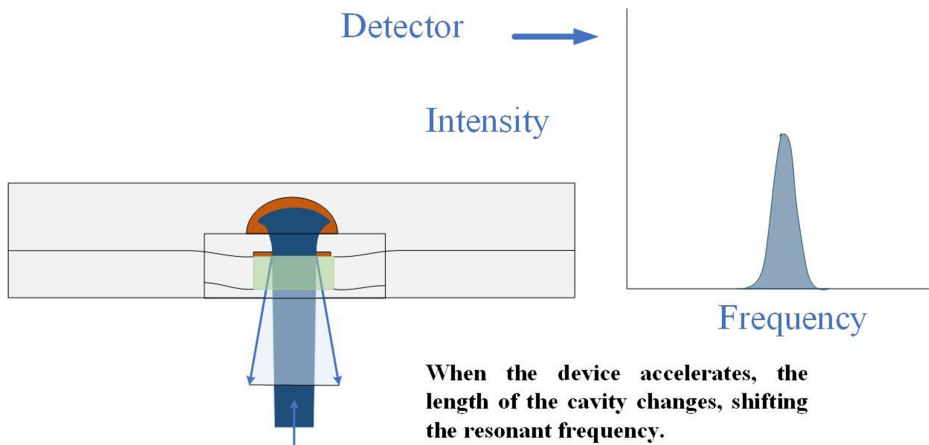


Figure 9.28. Function of an optomechanical accelerometer. Adapted from [35]. Image stated to be in public domain.

Questions

1. What advantages do sensors at the nanoscale offer and why?
2. Differentiate between a nanosensor and a transducer with an example.
3. With proper physics, explain two future nanosensor designs and their characteristics.
4. Do you think nanosensors have the capability to change warfare? Why and how?
5. Explain how graphene NEMS resonators work on the principle of resonance frequency? Give two applications of such a sensor.

6. Mention the challenges faced in developing and implementing nanosensor-based applications.
7. Name two commonly used nanosensors in today's state-of-the-art and describe how they are fabricated.

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