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Invited Paper

NANOSTRUCTURED AND NANOSCALE DEVICES AND SENSORS

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The dimensionality of a system has a profound influence on its physical behaviour, more specifically for nanostructured materials in which the size is comparable to the size of the fundamental physical quantities. Carbon based nanostructured materials exhibit unique mechanical, electrical, and optical characteristics, which may result in many unique device designs. The materials are biocompatible, chemically inert but capable of altering their electronic properties in the presence of some chemical species, and dimensionally compatible with biomolecules. They have interesting electronic characteristics, hence rendering them as potential chemical and biosensors. Recent heightened awareness of the potential for inadvertent or deliberate contamination of the environment, food and agricultural products has made decentralized sensing an important issue for several federal agencies. Recent progress in nanostructured materials and their possible applications in chemical and biological sensors could have a significant impact on data collection, processing, and recognition. Our present and ongoing investigation is aimed towards evaluating the applications of nanostructures of carbon and other materials in unique devices and sensors. Field emission in carbon nanotubes is used to detect environmental emission and atomic force microscopy and surface plasmon resonance are used for the detection of E-coli O157:H7 immobilized on layers of nanoparticles. Such devices display unique characteristics, morphological flexibility and biocompatibility.

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1. Introduction

The reduced dimensionality of a system has a profound influence on its physical behaviour. With the advances in technology over the past few decades, it has become possible to fabricate and study reduced-dimensional systems in which electrons are strongly confined in one or more dimensions. Recent revolutionary progress in the synthesis and characterization of carbon-based nanostructured materials and continuously emerging nanotechnologies has demonstrated tremendous potential for the development of new devices and sensor designs with unique capabilities [1]. Carbon-based nanostructures exhibit unique properties and morphological flexibility, rendering them inherently multifunctional and compatible with organic and inorganic systems. The applications of carbon nanotubes (CNTs) range from quantum wire interconnects [2], diodes and transistors for computing [3], high power electrochemical capacitors [4], data storage devices [5], field emitters for flat panel displays [6,7,8] and terahertz oscillators [9]. Successfully contacted CNTs have exhibited a large number of useful quantum electronic and low dimensional transport phenomena [10], such as true quantum wire behaviour [11], room temperature field effect transistors [3], room temperature single electron transistors [12], Luttinger-liquid behaviour [13], the Aharonov-Bohm effect [14] and

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Fabry-Pérot interference effects [10]. CNTs with aspect ratios of the order of 1000, coupled with a high conductivity, are ideal candidates for low voltage field emitters, with applications in CNT-based cold-cathodes for X-ray generation [15]. On a different yet related note, in clinical medicine, the current trend is to decentralize laboratory facilities and conduct clinical trials by employing direct-reading, portable, lab-on-chip systems. A heightened awareness of the potential for inadvertent or deliberate contamination of the environment, food and agricultural products has made decentralized sensing an important issue for several federal agencies. Recent progress in nanostructured materials and their possible applications in chemical and biological sensors could have a significant impact on data collection, processing, and recognition. A nanotechnology-based sensor platform will enable the direct detection of biological and chemical agents in a label-free, highly multiplexed format, over a broad dynamic range. This platform utilizes functionalized nanotubes, nanowires, and nanoparticles to detect molecular binding with high sensitivity and selectivity. The platform is capable of detecting a broad range of molecules, viz., DNA, RNA, proteins, ions and cells, and even the pH values. Detection is possible in both the liquid and the gas phase, and is highly multiplexable, allowing for the parallel detection of multiple agents. The work reported here presents nanostructured and nanoscale device designs and chem-bio sensor platforms.

2. Biosensors: Function, specificity and sensitivity

Biosensors are simple, inexpensive measurement systems that use biological molecules - usually enzymes, antibodies, or nucleic acids - to recognize simple molecules of interest via hydrogen bonding, charge-charge interactions and other biochemical interactions, and to provide molecular information. Recent advances in the field of nanotechnology and processing have resulted in solid-state biosensors offering unprecedented capabilities for genetic screening and detection. As compared to earlier catalyst system based biosensors, the next generation of affinity biosensors deliver real-time information about the antibodies to antigens, cell receptors to their glands, and DNA and RNA to nucleic acid with a complimentary sequence. Both types of sensor offer a multitude of applications, e.g., they can be used to measure blood glucose levels, to detect pollutants and pesticides in the environment, to monitor food-borne pathogens in the food supply, and to detect chemical and biological warfare agents. As an example, food safety has become one of the most critical issues in sensing, due to the zero-tolerance mandate for the presence of micro-organisms in foods. To be able to detect at one colony forming units (CFU)/ml sensitivity and to answer questions in molecular genetics, nanostructured and nanoscale devices offer distinct advantages, due to the dimensional compatibility, as shown in Figure 1 for a broad range of molecules.

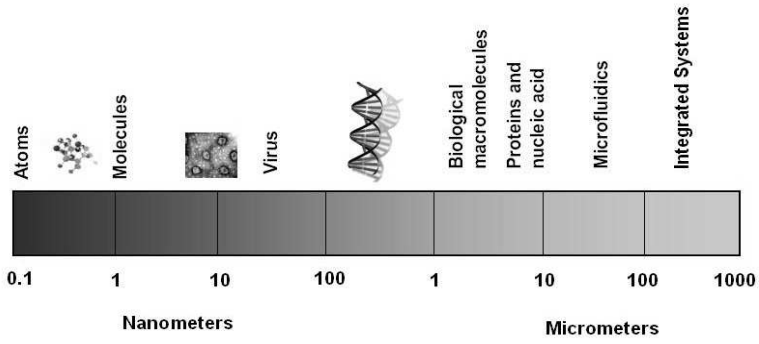

Fig. 1. Size and compatibility.

The conventional methods of pathogen detection require time-consuming steps to arrive at consequential data. Methods such as enzyme linked immuno-sorbent assay (ELISA) and polymerase chain reactions (PCR) have been employed for pathogen detection, because of their improved speed and reliability. However, they are time consuming as they require enrichment, isolation, morphological examination, biochemical and serological testing to positively identify pathogens. The times required for ELISA and PCR are from 10 to 28 hours and from 4 to 6 hours, respectively,

while the assay time for optical biosensors is around 2 hours under ideal conditions. An advantage of biosensors is their improved sensitivity compared to that of ELISA and PCR methods. An appropriate protocol could be developed for biosensors, employing immuno-detection principles, to significantly reduce the assay time as well as to detect smaller concentrations of bacteria with fewer false positives. Currently, tools are available to study the expression properties manifested by specific types of genetically modified plants at the molecular and nanoscale level. Studies of DNA and nucleotide based micro array expression patterns are beginning to explore signal transduction phenomena. Signalling genes are thus ideal candidates for their expression through chemically inducible promoters to be used in the development of various sensors. Recent progress in nanostructured materials, and their possible applications in chemical and biological sensors, could have a significant impact on data mining, recognition, and bio-informatics. Table 1 lists different types of sensor platform, their sensitivities, and a merit analysis.

Table 1. Different types of sensor, with their sensitivities, merits and drawbacks.

Type of Sensor	Advantages	Range	Disadvantages
Direct DNA electrochemistry	Highly sensitive. Requires no labelling step. Amenable to a range of electrodes.	10^{-15} m of target	High background signals. Cannot be multiplexed. Sample is destroyed.
Indirect DNA electrochemistry	Highly sensitive. Usually requires no labelling step. Multiple target detection at the same electrode.	10^{-18} m of target	Probe substrate can be difficult to prepare. Sample is destroyed.
DNA-specific redox indicator detection	Moderate to high sensitivity. Well suited to multiple-target detection. Samples remain unaltered.	10^{-15} m of target	Chemical labelling step required. Sequence variation may be problematic.
Nanoparticle-based electrochemistry amplification	Extremely sensitive. Well suited to multiple-target detection. Highly multiplexable.	$10^{-15} – 10^{-21}$ m	Many steps in assay. Reliability and robustness of surface structures problematic. Sample is usually destroyed.
Nanowire and nanoporous based detection	Extremely sensitive. Well suited to multiple-target detection. Highly multiplexable.	$10^{-15} – 10^{-21}$ m	Still in the development stage. Robustness yet not established. No prototype to date.
DNA-mediated charge transport	Highly sensitive and simple assay. Requires no labelling. Suitable for mismatch detection. Sequence independent. Multiplexable. Applicable to DNA-protein sensing.	10^{-15} range	Biochemical preparation of target sample required.

2.1. Carbon nanotubes, nanowires and nanoparticles

CNTs are conducting, can act as electrodes, generate electro chemiluminescence (ECL) in aqueous solutions, can be derivatized with a functional group that allows immobilization of biomolecules, have high surface-to-volume ratios for adsorption, and have surface-to-weight ratios ~ 300 m^2g^{-1}. The uniform chemical functionalization of CNTs is a key step in the formation of biosensors. Oxidation of nanotubes with HNO_3-H_2SO_4 leads to high concentrations of carboxylic, carbonyl, and hydroxyl groups on the surface, and removal of the tip to expose the tube interior. Carboxyl groups can readily be derivatized by a variety of reactions allowing linking of biomolecules such as proteins, enzymes, DNA, or even metal nanoparticles. The covalent

modification of nanotubes facilitates the creation of well-defined probes, which are sensitive to specific intermolecular interactions of many chemical and biological systems. Integration of the transducer and probe enables quick, accurate, and reversible measurement of target analytes without the use of reagents, unlike multi-step conventional assays that may require sample treatments and are often irreversible. By using sequence specific-attachment, nanotube-based electronic devices with specific molecular-recognition features of DNA have been reported [16]. Such probes are useful for imaging self-assembled monolayers (SAM) and biological systems.

The possibility of covalent modification of SWNTs offers mapping of functional groups at a true molecular resolution. Furthermore, chemical processes to link catalysts, such as transition-metal complexes, to the ends of CNTs are useful in creating or modifying the structures at a molecular scale, creating interconnections for electronic devices, and even developing new classes of materials. Covalent functionalization of the sidewalls of SWNTs provides stability and the best accessibility, but at the expense of damaging the sidewalls, thereby diminishing the mechanical and electronic properties. However, non-covalent routes to nanotube functionalization offer ease of synthesis and minimum disruption of the tubular structure. As an example, non-covalent functionalization of a SWNT by application of a polymer wrapping around it provides an electrically non-interactive baseline, while the reactive groups of the polymers allow for interaction with specific molecules. When these interact with the polymer coatings, the electrical properties of the nanotubes are altered, enabling detection of the molecules. This provides an extremely sensitive sensing mechanism.

In addition to nanotubes, novel materials such as porous silicon [17] and porous carbon [18], with porosities of comparable dimensions to those of the biomolecules, have been used for biosensor applications, with limited success. The mesoporous carbon matrix is used for stable immobilization of the biological molecule, and C_{60} serves as an electron mediator. Both C_{60} and nanotubes have been shown to be good electron mediators when used with a mesoporous carbon matrix or modified metal electrodes. CNT-based transducers, however, show a significant advantage over porous silicon due to the well defined, defect free, structures and also because the nanotubes promote homogenous electron transfer reactions. Surface characterization and chemical selective imaging techniques can be used as biosensors at the nanometer scale, employing one of two approaches for surface patterning, viz., functionalization of conventionally patterned surfaces with robust SAMs and subsequent addition of the biomolecules, or direct patterning of the surface with biological molecules. Our current investigation involves the development of proof-of-concept sensors, fabricated employing nanostructured materials as a first systematic attempt to advance a novel concept of sensor development, not only for the food and agriculture industry but also for applications including high-throughput genetic analysis, proteomics, drug screening, clinical diagnostics and bio-warfare agent detection.

2.2. Sensors and devices

In a typical CNT-based device, nanotubes connect two metal electrodes and the conductance between them can be measured as a function of gate bias voltage. Since the electrical characteristics are influenced by the atomic structure; changes such as mechanical deformation and chemical doping induce changes in conductance, thus rendering such devices sensitive to their chemical and mechanical environment. It has been demonstrated that chemical sensors based on an individual or ensembles of SWNTs can detect 200 ppm of NO_2 and < 2% of NH_3 in a few seconds [19]. Hence, sensors made from SWNTs have high sensitivities and fast response times, even at room temperature. First principles calculations using density functional theory (DFT) on molecules, such as CO, NH_3, NO_2, O_2 and H_2O, show the direction of the charge transfer and hence doping of the semiconductor tube [20]. For H_2O, a simulated molecular configuration shows a repulsive interaction, indicating no charge transfer in presence of the water molecule [21]. This offers an important option for using SWNTs in water as biochemical sensors. Conventional ionisation gas sensors work by detecting the ionisation characteristics of gases, but are limited by the size and high voltage operation, rendering CNT-based gas sensors as attractive alternatives.

SWNTs and MWNTs are found to be excellent field emitters [22], at relatively low operating voltages in comparison to devices based on thermionic emission. In Spindt-type and diamond tip emitters, the electron emission from such sources offers a robust and viable alternative due to the large aspect ratio, structural integrity, high electrical and thermal conductivity, chemical stability, and the possibility of large-scale production. Recently, there have been studies of the

utilization of CNTs as field emitters for display panels, as cold-cathodes for X-ray generation, and in photonic devices. Although the field emission currents from either aligned or randomly oriented single carbon nanotubes have been extensively studied, a systematic and thorough investigation is indispensable as field emission depends strongly on morphology, diameter, spatial distribution, alignment, and the contact between the CNT and substrate, as well as the condition of the CNT tip. The emission current from a metal surface is determined by the Fowler-Nordheim (F-N) equation,

$$I = aE_{apl}^{\ 2} \exp(-b\phi^{3/2} / \beta E_{apl}) \tag{1}$$

where I, E_{apl}, ϕ, and β are the emission current, applied field, work function, and field enhancement factor, respectively. For metals with typical work functions, the threshold field is prohibitively high, around 10^4 V/μm. Field emission sources rely on the field enhancement factor due to sharp tips/protrusions, such that they tend to have smaller virtual source size because of the role of the β factor. The larger the β factor, the higher the field concentration and the lower the effective emission threshold voltage. A change in the electronic structure of the nanotube caps can affect the field emission current and its temperature dependence. DFT calculations indicate that the large electric field present at the tip during the electron emission condition helps stabilize the adsorbates and lower the ionisation potential, furthering electron emission. We investigated electron emission from carbon nanotubes in a vacuum, and its onset occurred at an electric field of 1.45 V/μm. An emission current of 0.35 mA was observed at an electric field of 3.8 V/μm, which represents a very large current density, close to the theoretical limit for resistive heating. Our reported values of $E_{to} \cong 4.85$ V/μm and $E_{thr} \cong 14$ V/μm are consistent with those in the literature [23]. The field amplification factor β was estimated to be around 850 from the I-V and F-N plots. For this consideration, a simplified formula by Brodie and Spindt [24] was employed, viz.,

$$I=A\frac{1.5*10^6}{\Phi}E^2_{Apl}\beta^2\exp\left(\frac{10.4}{\sqrt{\Phi}}\right)\exp\left(\frac{-6.44*10^7\Phi^{1.5}}{E_{Apl}\beta}\right) \tag{2}$$

The work function for a catalytic MWNT has been reported to be 5.3 eV [25]. Studies leading to emission stability, tip longevity, and triple junctions to boost emission are currently under investigation. CNTs can emit very large electron currents for extended periods of time, without any catastrophic failure. Under an applied electric field, the CNTs tend to align themselves in its direction. SWNTs have smaller diameters and have demonstrated a stable emission current ~ 2 μA, corresponding to a current density of 10^8 A/cm^2. CNT field emitting surfaces can be printed or even painted with nanotubes, or even grown in-situ. Recently, a low threshold field ~ 1.6 - 2.6 V/μm was reported for MWCNTs and boron doped MWCNTs embedded in a polystyrene matrix [26]. Free-standing CNTs often provide non-uniform current distributions and limited current stability due to mutual shielding, residual pressure and heating effects. To improve the field emission stability, approaches such as the synthesis by MOCVD of massive arrays of mono-dispersed CNTs in a porous silica template, and growth using a single mask self-aligned process with an integrated gate electrode are used [27]. The existence of very large fields at the CNT tips, even at very low voltages, could produce compact, battery powered gas ionisation sensors. Such sensors are expected to show good sensitivity and selectivity, and to be unaffected by extraneous factors such as temperature, humidity and gas flow. CNTs have demonstrated an electric field induced change in their bandgaps, which is interesting as it will lead to the detection of ionic species without inducing charge transfer or doping of SWNTs.

For the present investigation, SAM based surface plasmon resonance (SPR) and Atomic Force Microscopy (AFM) techniques were used to detect pathogens. The SPR detection technique is rapid, real-time, and requires no labelling, as compared to the detection of pathogens by PCR based techniques, which may require sample preparation, fluorescent labelling, and longer times to arrive at a quantitative conclusion. SPR involves immobilizing antibodies by a coupling matrix on the surface of a thin film of precious metal, such as nanoparticles of gold deposited on the reflecting surface of an optically transparent wave-guide. The precise angle at which SPR occurs depends on several factors. One of the main ones is the refractive index of the metal film, to which target molecules are immobilized using specific capture molecules or receptors along the surface, that

cause a change in SPR angle. This can be monitored in real-time by detecting changes in the intensity of the reflected light, producing a sensorgram. The rates of change of the SPR signal can be analysed to yield apparent rate constants for the association and dissociation phases of the reaction. When the antigens interact with antibodies, the refractive index of the medium surrounding the sensor changes, producing a shift in the angle of resonance. This change is proportional to the change in the concentration of antigens bound to the surface. Efforts are under way to enhance the sensitivity of such AFM- and SPR-based sensors.

3. Results

Figure 2(a) shows an AFM image of a rod shaped *Escherichia coli*, (b) shows a depth profile, and (c) shows the pathogen bound to its corresponding antibody on a SAM-based gold chip. As an example of the first patterning methodology, alkanethiol-type molecules can be used to selectively pattern gold surfaces. To investigate the capability of a SAM-based SPR biosensor for pathogen detection, various experiments were conducted. Immobilization using *E. coli* O157:H7 polyclonal antibodies suspended in NaOAc (pH 5.5) produced a pixel change of 12, while *E. coli* O157:H7 (pH 7.4) polyclonal antibodies suspended in PBST produced a pixel change of 7. Medina *et al.* [28] and Fratamico *et al.* [29] have also reported a higher response during immobilization at a pH of 5.0 than at one of 7.4. The SPR Instrument response during immobilization of antisera is shown in figure 3 (a). Increasing the concentration of the antigen in direct assay resulted in an increased response. In passing the antigen sample at a concentration of $4x10^8$ CFU/ml for 10 min, a change in the pixel value of 0.1 was noted while a concentration of $7x10^9$ CFU/ml produced an average change of 0.1667. One pixel change is equivalent to a 0.006º change in angle. For the same concentrations of antigens and different concentrations of secondary antibodies (1, 2, and 3 μL/ml) in sandwich assay, the response obtained was at least 30 times higher than for direct assay. A typical sensorgram for the sandwich assay is given in figure 3(b).

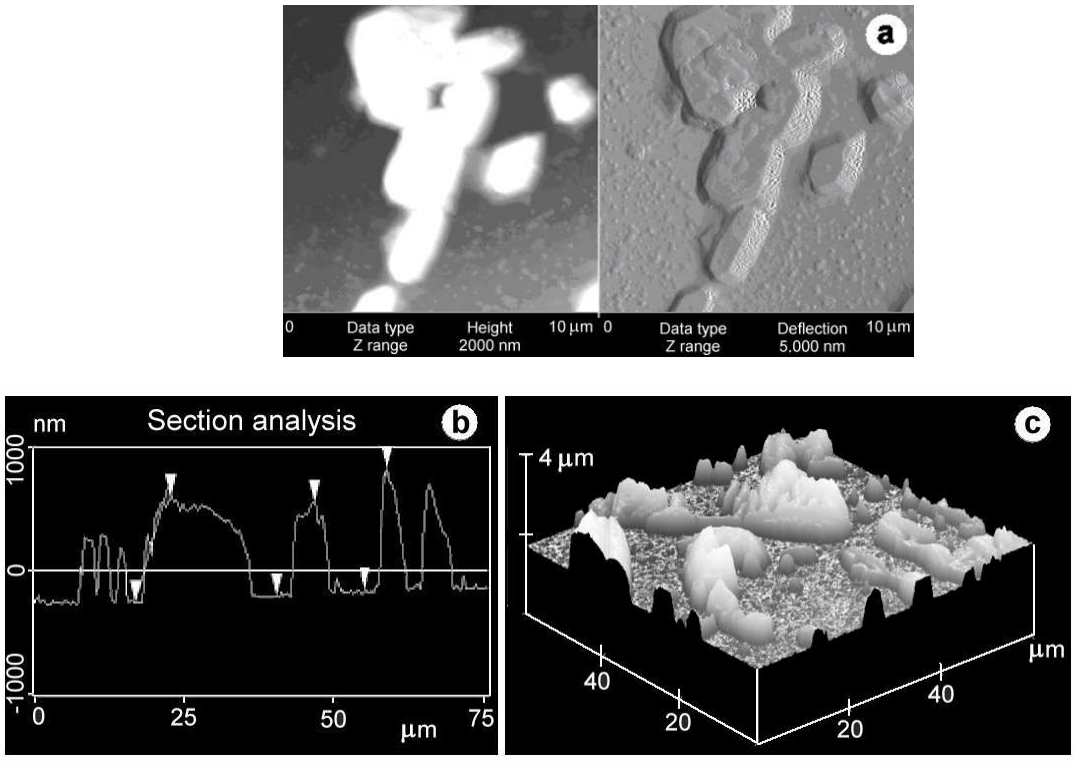

Fig. 2. (a): *E. Coli* O157:H7 on a gold chip. (b): A depth profile image of *E. coli* O157:H7 on a gold chip. (c): *E. Coli* O157:H7 bound to its antibody on a surface activated gold chip.

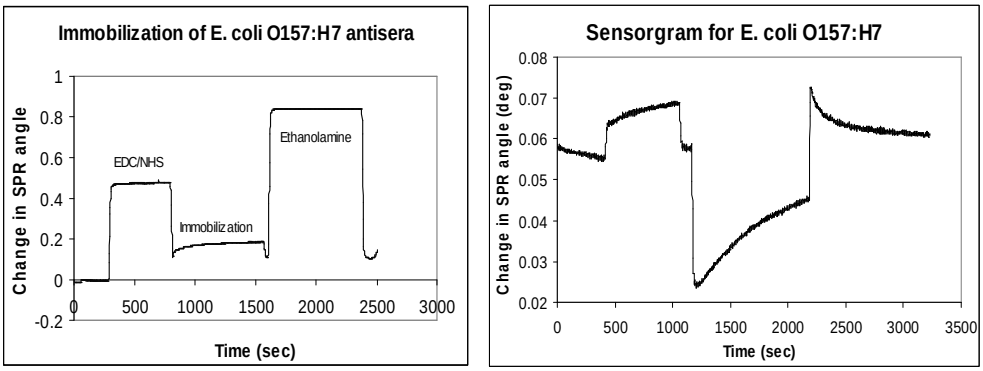

Fig. 3 (a). Immobilization of *E. coli* O157:H7 antisera. 275- 875 s: activation using EDC/NHS, 900 - 1500 s: immobilization of antibodies, and 1550 - 2400 s: ethanolamine. (b). Sensorgram for *E. coli* O157:H7. 450 - 1050 s: direct assay, 1200 – 2200 s: association, and 2200 - 3200 s: dissociation using NaOH.

4. Next-generation devices and applications

Since electron field emission in CNTs is possible at relatively low temperatures and voltages, X-ray tubes that can generate a sufficient X-ray flux for diagnostic imaging applications have been reported [30]. Such devices can produce focused electron beams with a very small energy spread, programmable pulse width and repetition rate, leading to the possibility of portable and miniature x-ray sources. Other futuristic applications include lamps with lifetimes > 8000 hours, nanotube-based gas discharge tubes for the protection of telecommunication networks against power surges, and microwave generators. One of the most remarkable characteristics is the possibility of bandgap engineering by controlling the microstructure. A pentagon-heptagon defect in the hexagonal network can connect a metallic to a semiconductor nanotube, providing an Angstrom-scale heterojunction with a device density ~ 10^4 times greater than currently possible.

Ferromagnetically filled CNTs usually exhibit coercivities greater than that of the bulk metal [31]. Fe-filled CNTs provide distinct magnetic properties such as an easy axis of magnetization perpendicular to the substrate plane and an enhanced coercivity. Owing to the nanoscale dimensions of the CNTs, this development offers a significant potential for the storage of data at approximately 20-40 GB/cm^2 capacities. Other possible applications of nanostructured composites include a superconductor with a record room T_c; a phonon quantum generator of hyper-sound with an extremely high frequency; a noiseless and loss-less super-frequency nanoantenna [32]; a solar cell with a record efficiency [1], and many other unique applications in photonics.

Research is currently in progress to fabricate nano-materials by integrating nano-fabrication and chemical functionalization, particularly in the case of nano-electrode assemblies interfaced with biomolecules for the development of biosensors. DNA molecules are electro-active at certain potentials that can be used to identify the hybridisation process. These sensors will be integrated into the next-generation `gene-chips', especially where detection of less than an attomolecule is critical. The recent discovery of quantum confined particles or quantum dots (QDs) having unique optical and electronic properties, such as size and composition-tunable fluorescence emission from visible to infrared wavelengths, a large absorption coefficient across a wide spectral range and a very high level of brightness and photo-stability, will lead to the development of multifunctional nanoparticle probes for cancer targeting and real-time in-vivo imaging in living cells. The broad excitation profiles and narrow, symmetric, emission spectra in high quality QDs are well suited to optical multiplexing, in which multiple colours and intensities are combined to encode genes, proteins, and small molecule libraries [33]. In-vivo studies show that QDs accumulate at tumour sites. Such QDs were encapsulated with triblock copolymers and treated chemically with tumour-targeting ligands having drug-delivery functionalities [34]. Other nano-technology projects include a nanoscale barcode for genome-wide screening such as disease susceptibility and therapeutic responses, and blood fingerprinting. CNTs are ideal building blocks for the fabrication of nano-devices that are not easily achievable using other materials.

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