2017

Carbon Nanomaterials and their application to Electrochemical Sensors: A review

Aoife Power
Central Queensland University

Shaneel Chandra
Central Queensland University

Brian Gorey
Technological University Dublin

James Chapman
Central Queensland University

Recommended Citation

Power, A., Chandra, S. & Gorey, B. (2017). Carbon Nanomaterials and their application to Electrochemical Sensors: A review. *Nanotechnology Reviews*, vol. 7, no. 1. doi.org/10.1515/ntrev-2017-0160

Carbon nanomaterials and their application to electrochemical sensors; A review

Article *in* Nanotechnology Reviews · January 2017

DOI: 10.1515/ntrev-2017-0160

4 authors:

Aoife C Power
Central Queensland University
19 PUBLICATIONS **66** CITATIONS
SEE PROFILE

Brian Gorey
Dublin Institute of Technology
7 PUBLICATIONS **19** CITATIONS
SEE PROFILE

Shaneel Chandra
Central Queensland University
32 PUBLICATIONS **40** CITATIONS
SEE PROFILE

James Chapman
Central Queensland University
46 PUBLICATIONS **202** CITATIONS
SEE PROFILE

Nanotechnology Reviews ‘Just Accepted’ Papers

Nanotechnology Reviews (Nanotechnol Rev) ‘Just Accepted’ Papers are papers published online, in advance of appearing in the layouted final online and print versions of the journal. The papers have been peer-reviewed and/or approved for publication by the Editors and are online published in manuscript form, but have not been copy edited, typeset, or proofread. Copy editing may lead to small differences between the Just Accepted version and the final version. There may also be differences in the quality of the graphics. When papers do appear in print, they will be removed from this feature and grouped with other papers in an issue.

Nanotechnol Rev ‘Just Accepted’ Papers are citable; the online publication date is indicated on the Table of Contents page, and the article’s Digital Object Identifier (DOI), a unique identifier for intellectual property in the digital environment (e.g., 10.1515/NTREV-2011-xxxx), is shown at the top margin of the title page. Once an article is published as **Nanotechnol Rev ‘Just Accepted’ Paper** (and before it is published in its final form), it should be cited in other articles by indicating author list, title and DOI.

After a paper is published in **Nanotechnol Rev ‘Just Accepted’ Paper** form, it proceeds through the normal production process, which includes copy editing, typesetting and proofreading. The edited paper is then published in its final form in a regular print and online issue of **Nanotechnol Rev.** At this time, the **Nanotechnol Rev ‘Just Accepted’ Paper** version is replaced on the journal Web site by the final version of the paper with the same DOI as the **Nanotechnol Rev ‘Just Accepted’ Paper version.**

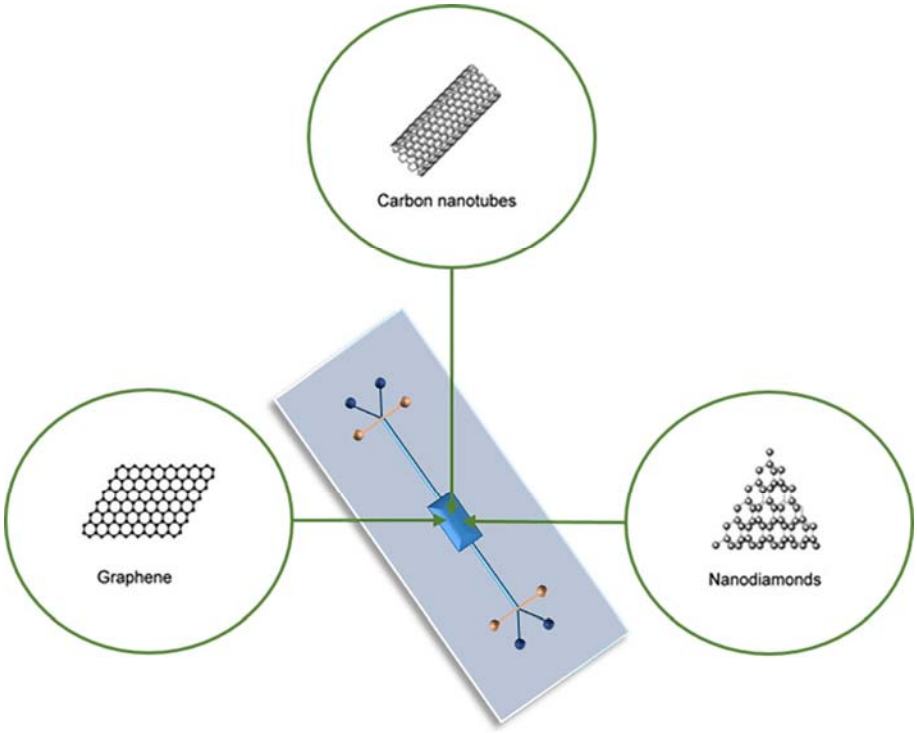
Disclaimer

Nanotechnol Rev ‘Just Accepted’ Papers have undergone the complete peer-review/approval for publication process. However, none of the additional editorial preparation, which includes copy editing, typesetting and proofreading, has been performed. Therefore, there may be errors in articles published as **Nanotechnol Rev ‘Just Accepted’ Papers** that will be corrected in the final print and online versions of the Journal. Any use of these articles is subject to the explicit understanding that the papers have not yet gone through the full quality control process prior to advanced publication.

Graphical abstract

Carbon nanomaterials and their application to electrochemical sensors; a review

A.C. Power, B. Gorey, S. Chandra, J. Chapman



A review of the current application of carbon nanomaterials in electrochemical sensors.

Nanotechnology Reviews **'Just Accepted' paper**
ISSN (online) 2191-9097
DOI: 10.1515/ntrev-2017-0160

Review

Carbon nanomaterials and their application to electrochemical sensors; a review

A.C. Power[1], B. Gorey[2], S. Chandra*[1], J. Chapman[1]

[1]The Agri-Chemistry Group, The Department of Agriculture, Science and Environment, School of Health, Medical and Applied Sciences, Central Queensland University, Rockhampton, 4701, Queensland, Australia

[2]FOCAS Institute, Dublin Institute of Technology, Camden Row, Dublin 8, Ireland

*Corresponding author

e-mail: s.chandra@cqu.edu.au

Abstract

Carbon has long been applied as an electrochemical sensing interface owing to its unique electrochemical properties. Moreover, recent advances in material design and synthesis particularly nano materials, has produced robust electrochemical sensing systems that display superior analytical performance.

Carbon nanotubes (CNTs) are one of the most extensively studied nanostructures because of their unique properties. In terms of electroanalysis, the ability of CNTs to augment the electrochemical reactivity of important biomolecules and promote electron-transfer reactions of proteins is of particular interest. The remarkable sensitivity of CNTs to changes in surface conductivity due to the presence of adsorbates permits their application as highly sensitive nanoscale sensors. CNT-modified electrodes have also demonstrated their utility as anchors for biomolecules such as nucleic acids, and their ability to diminish surface fouling effects. Consequently, CNTs are highly attractive to researchers as a basis for many electrochemical sensors.

Similarly, synthetic diamonds electrochemical properties, such as superior chemical inertness and biocompatibility, make it desirable for both (bio) chemical sensing and as the electrochemical interface for biological systems. This is highlighted by the recent development of multiple electrochemical diamond based biosensors and bio interfaces.

Introduction

Electrochemical analysis is a simple, cost effective method to quantitatively and qualitatively determine the levels of electroactive species in a solution. Advantages of electroanalytical techniques over other detection methods such as chromatography, luminescence and spectroscopy are their low cost, ease of use, accuracy and reliability. Varieties of techniques are available to researchers to study the electrochemistry of electroactive species in solution. Analytical techniques employed include cyclic voltammetry, differential pulse voltammetry, chronoamperometry, linear sweep voltammetry and stripping voltammetry. All of them are effective electroanalytical techniques after being optimised to obtain the best electrochemical response. These processes can be influenced by several factors, including the nature of the analyte under investigation, the type of electrode and the choice of electrolyte. Specifically, the size and morphology of the electrode and the fabrication method used can be influential on the voltammetric response of the system [1].

Procedures in electroanalysis strongly depend on material aspects such as chemical and physical properties of electrode surfaces, the effects of the applied potential, adsorption, and coatings applied to the electrode surface to enhance detection. Carbon materials such as those depicted in figure 1, are widely used in electroanalytical investigations because of their chemical inertness, relatively wide potential window, low background current, and suitability for different types of analysis. For example, other electrode materials, such as sputtered metal electrodes, exhibit reduced potential windows and lifetimes in comparison to carbon materials [2].

Carbon nanomaterials, such as, graphene, carbon nanotubes (CNTs), crystalline diamond, and diamond-like carbon, all display exceptional electrochemical properties which has resulted in their widespread application. The potential of these materials is unquestionable in sensing applications, as the novel carbon-derived nanomaterials possess properties that are unfathomable in bulk materials. This results in their capability to operate with not only a higher sensitivity and selectivity in harsh environments but also over greater temperature and dynamic ranges. Historically, a number of materials including platinum, gold, and various forms of carbon have been exploited as electrode materials for electrochemical detection [3-7]. Graphene, CNTs and diamond are the polymorphs of carbon that have been widely employed as electrode materials for electrochemical sensing in recent years. Consequently, this review focuses on the recent (< 5 years) incorporation and use of carbon-derived

nanomaterials for electrochemical sensing applications and their potential implications. Moreover, as the excellent properties of carbon nanomaterials, such as large surface–to–volume ratio, high conductivity and electron mobility at room terature, have led to numerous advances in electrochemical sensors. This review aims to highlight the application of carbon based sensors in multiple fields as electrochemical sensors for DNA, proteins, pollutants, metal ions, gases, and immunosensors.

The impact of the discovery of the C60 bucky-ball by Smalley *et al.* [8], coupled with the emergence of an additional carbon crystal structure alongside graphite and diamond, led to the development of CNTs by Iijima group [9]. From their discovery in the early 1990s CNTs have attracted significant attention in multiple disciplines including physics [10], chemistry [11-13] and materials sciences [14, 15], an interest that has yet to wane. The interest in CNTs is due to their chemical stability and distinguishing mechanical and electronic properties. These features are ultimately a product of their distinct structure compared to that of traditional carbon fibres and graphite. CNTs possess a cylindrical structure produced from hexagonal "honeycomb' lattices fabricated from sp^2 carbon units. This lattice structure results in a closed topology with nanometre diameters and lengths in the micron range. CNTs consist of two defined structural groups single- (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) [16, 17]. SWCNTs are comprised of a 1 – 2 nm diameter closed graphite tube rolled (seamless) from an individual graphite sheet, whereas MWCNTs are the product of the "Matryoshka" like nesting of multiple individual graphite cylinders with diameters typically ranging from 2 to up to 25 nm and a gap between tubes similar to the interlayer spacing in graphite of approximately 0.34 nm [18]. The influence of CNT structure is particularly evident in their electrical behaviour, where depending on their helicity (symmetry of the two-dimensional carbon lattice) and diameter, they act in a fashion similar to that of a semiconductor or metal [19-22].

The electronic properties of CNTs, particularly SWCNTs, are well-defined and are known to exhibit comparable characteristics to quantum dots and wires at low temperatures including single-electron charging and Coulomb blockade [23-26]. Coupling these features with the additional favourable properties inherent to nanostructures, such as high surface to volume ratios, unique confinement effects and altered (from the bulk) physical and chemical properties [27], have resulted in wide ranging applications. The high number of applications is due to enhanced selectivity, sensitivity and faster electrochemically reversible responses at standard temperatures and pressure. Applications include but are not limited to chemical

sensors [28-32], catalyst scaffolds [33-36], energy storage and conversion [27, 31, 37] and electronic devices [25, 38, 39].

Additionally, when CNTs are used as electrodes in electrochemical reactions, they display greater electron transfer capabilities [40]. Moreover, they possess significant potential as biosensors due to their ease in supporting protein immobilisation while maintaining the proteins inherent activity [41, 42]. CNTs have been exploited in multiple electrochemical sensors because of their ability to facilitate electron transfer reactions with electroactive species in solution and the electrode interface [43-46].

The literature indicates that CNTs demonstrated better behaviour than materials traditionally used as electrode interfaces which display good conductivity and chemical stability. Electrochemical transducers that exploit CNTs as substrates offer significant improvements in the performance of amperometric enzyme electrodes [47, 48], immunosensors [49, 50] and nucleic-acid sensing devices [51, 52] because of their increased sensitivity and improved signal-to-noise ratio. CNT – modified electrode interfaces are highly attractive for a myriad of amperometric oxidase and dehydrogenase based biosensors because of the augmented electrochemical reactivity of species such as nicotinamide adenine dinucleotide (NADH) [53-55] and hydrogen peroxide [56, 57]. CNT based transducers have been shown to amplify bio-catalytic reactions and provide a platform for multiple enzyme tags. When aligned as "forests", CNTs often act similarly to molecular wires, providing enhanced electron transfer between the underlying electrode and the enzymes redox centre [58-62]. The unique properties of CNTs have resulted in their exploitation in a range/multitude of diverse fields including sensors [40, 63, 64], actuators [40, 65] and energy storage [66, 67].

As the resistivity of conducting materials is dependent on the number of electron carriers available and the potential availability of electrons and electron holes, the semi-conducting nature of graphite is a result of the free movement of the π-electrons above and below the hexagonal graphene layer. On the other hand, the unique electrical properties of CNTs are a product of the π – bonding between the carbon atoms and their quasi – one-dimensional shape. This is a consequence of the defined circumference of the nanotubes, which limits the number of potential electron states. As a consequence, the semi – metal nature is altered, resulting in the opening of a band gap at the Fermi energy level. For CNTs with larger diameters, the potential band gap decreases as the spacing between the graphene layers decreases. Therefore, electron transfer can occur without scattering over relatively large

distances of several micrometres depending on the mechanical quality of the nanotubes [68-70]. Electron transfer is primarily driven by the conducting states available along the CNT structure with each conducting state providing a quantum conduction via the transportation of one spin up and one spin down electron/hole. However, because of significant reflection at the CNT – contact interface, which is a result of difficulties in accessing the various electron states; a consequence of their reduced numbers and specific configurations. This is because the number of transmitted electrons or holes is dependent on the amount of available states. Overall, this causes the drop in voltage conducted through both metallic and semiconducting CNTs across the CNT contacts but not along the tube itself [70, 71].

Moreover, coupled with the non-scattering 'ballistic' electron transfer, the mechanical robustness of CNTs allows them to withstand current densities up to $10^{10}Acm^{-2}$, which is ~3-4 orders of magnitude higher than most metals [41, 72, 73]. Consequently due to their attractive electrical properties, CNTs have long been considered a potential alternative for silicon – based circuits [74-76] and they have many promising applications in the field of nano-electromechanical systems [77-79]. Individual nanotubes can be utilised to fabricate transistors and the connections between transistors in integrated circuits because of their capability to act as either metallic- or semi- conductors [80, 81]. This is highly advantageous as the miniaturisation of conventional metal oxide semiconductors silicon transistors are fast approaching fundamental physical limits [82, 83]. The potential implementation of CNT – based circuits affords the potential continued miniaturisation of transistor dimensions is an essential factor for improved integrated circuit performance and the potential implementation of CNT – based circuits [83].

Diamond

The potential of diamond as an electrochemical transducer has attracted remarkable interest due to its chemical stability, wide potential window, low background current and bio-compatibility [53, 84-86] of other commonly exploited materials such as silicon (Si) [87, 88], silicon dioxide (SiO_2) [89, 90], tin dioxide (SnO_2) [91, 92], gold (Au) [93, 94] and glassy carbon [95, 96]. High-quality diamond films typically possess a potential window of $\geq$ 3.25 V, owing to the large over-potentials for both oxygen and hydrogen evolution [97, 98] as a result of diamond to be either insulating, semiconducting or metallic, with its appearance

moving from transparent to black (optical gap of 5.47 eV), as a result of diamonds ability to be either p- or n-type doped [97-99].

Diamond interfaces demonstrate distinctive properties because the electronic properties can be optimised by termination with either oxygen, hydrogen or hydroxide groups [99]. When terminated with hydrogen the surface is hydrophobic [100, 101]. In contrast, when oxygen is used for termination the surface is inherently hydrophilic [102]. Despite diamond being renowned for its bio – compatibility, chemical inertness and DNA bonding stability, the application of diamond in chemical sensors or electronics has yet to be properly exploited. This lack of use was due to the associated high cost of their production and refinement. The development of methodologies to cost effectively fabricate nano – crystalline diamonds, which display properties that are interchangeable with properties of a single crystal diamond, has opened up multiple avenues for future research in the development of innovative products for a multitude of potential applications [103-105]. For example, Petrakova and colleagues developed a non-toxic nanoscale diamond carrier which demonstrated simultaneous transfection of cells and spatiotemporal fluorescence imaging of DNA without the need for DNA labelling. The system was based on fluorescent nano-diamond particles coated non-covalently with polyethylenimine. This can form reversible complexes with DNA as detailed below in Figure 2, section a of which illustrates the electrostatic formation of the fluorescent nano-diamond – polyethylenimine –DNA complex, this involves the negatively charged nanodiamond interacting with the positively charged polyethylenimine, which in turn complexes the DNA, once the complex penetrates the target cell the DNA is then released.

Diamond-like carbon

Carbon can crystallise in both sp^2 graphite and sp^3 diamond forms, the majority of which are chemically very stable. Consequently, under static conditions, they can be considered as inert species. Both can interact with liquids or gases in a manner defined by the influence of sliding contacts, such as terminating bonds at the interface. Diamond-like carbon (DLC), amorphous carbon or amorphous hydrogenated carbon is a non – crystalline carbon with a high percentage of diamond – like (sp^3) bonds. Hydrogen-free DLC thin films have an increased fraction of sp^3 configuration and are fabricated by either filtered cathodic vacuum arc, pulsed laser deposition, or mass selected ion beam deposition [106-109]. Alternatively, sp^2 configured hydrogenated amorphous carbon fabricated via plasma enhanced chemical

vapour deposition or reactive sputtering techniques [110-113]. The presence of sp^3 bonding is safeguarded by ensuring the deposition flux is made up of a high percentage of medium energy ions (approx. 100 eV) [114].

Recently, DLC films have emerged as an area of significant interest for certain electrochemical applications. This interest is a result of characteristic and desirable properties being realised; such as mechanical hardness, low surface roughness, enhanced elastic modulus and chemical inertness, as well as its semiconductor nature, with a tuneable band gap of 1 to 4 eV (approximately) [115].

Nitrogenated DLC films have been exploited as both electrochemical probes for trace metal analysis and as coatings for glucose oxidase biosensor selective membranes [116-119]. DLC probes have been reported as glucose biosensors [86, 120, 121] and as microelectrode based probes for multiple medical applications [106, 122-125].

The sp^3- carbon/sp^2 hybridisation ratio of the DLC interface may be adjusted and controlled depending on the deposition process and conditions. DLC can also be doped to form conductive/semi – conductive materials to tailor them to a specific application, whether that be electronic [126], optical [127], mechanical [128] or biomedical [129] applications.

CNTs for chemical sensing

Electrochemical sensors based on CNTs

With the advent of nanotechnology came the capability to manipulate at the atomic level and synthesise uniquely organised molecular structures. In the last few decades, CNTs have been the focus of intense research because of their remarkable mechanical and electronic properties coupled with their chemical stability and heat conduction [25, 130-132]. Diamond (the hardest natural material) is an insulator and graphite is one of the softest conducting materials in nature. The electronic properties of CNTs are unique to the carbon family because of the unique atomic structure (– large surface to volume ratios with diameters of a few nanometres and lengths of up to 100 μm, forming extremely thin wires that possess the hardness of diamond and the conductivity of graphene –) and mechanical deformations which make them useful in the development of miniaturised sensors that are sensitive to chemical, mechanical and physical environments [59, 78, 133]. Electrochemical sensors are composed

of an electrochemical cell which incorporates a minimum of two electrodes to form a closed electrical circuit and a transducer where the charge transport (which is always electronic) occurs, whereas, the charge transport in the analyte sample can be either electronic, ionic, or mixed. CNTs electronic properties are a consequence of the graphene sheets curvature. Carbons electron clouds are transformed from a uniform distribution along the C–C backbone in graphite to an asymmetric distribution within and around the cylindrical sheet of the nanotube. A rich π-electron conjugation forms outside the tube as a result of the electron clouds distortion making the CNT electrochemically active [63, 134-136]. Doping SWCNTs with electron donating and withdrawing molecules such as NO_2, NH_3, and O_2 either transfers electrons to or withdraws electrons from SWCNTs, giving the SWCNTs more charge carriers or holes, in turn increasing or decreasing their conductance [137].

It has been shown not only can the electrochemical reactivity of important biomolecules be enhanced by CNTs [138-140], but the electron transfer reactions of proteins can also be promoted [141, 142]. CNT modified electrodes have demonstrated the capability to alleviate surface fouling which can occur, for example, in the case of direct oxidation of NADH due to the high over-potentials required, which result in fouling of the electrode surface by oxidation products [138]. Moreover, CNTs accumulate important biomolecules such as nucleic acid [143-145] which aids in the enhancement of the probes selectivity and sensitivity. In order to exploit CNTs in electrochemical sensing applications it is essential that the CNTs be appropriately functionalised [146-148] and immobilised [139, 149].

Most commonly, CNTs are confined onto electrochemical transducers by coating electrode substrates with CNTS [10, 39, 150] or by incorporating them into composite electrodes [136, 151, 152]. While CNTs have played a significant role in enhancing the performance of electrochemical biosensors, such as enzyme electrodes, DNA biosensors and immunosensors [136] they have also demonstrated potential in electrochemical detection for various separation techniques including high-performance liquid chromatography [153, 154] and capillary electrophoresis [155, 156].

The electrochemical functionalisation of CNTs with metallic nanoparticles and the application of the resulting metal decorated CNTs has also seen increased interest in recent years particularly in areas related to sensing and catalysis [157-160]. For example, Wang *et al.* designed a one-pot hot-solution synthesis method for $Ni_{12}P_5$/CNTs hybrid nanostructures illustrated in figure 3. Hybrid structures attained current densities of 2 and 10 mA cm^{-2} when

over-potentials of just 65 and 129 mV were applied. In conjunction, the hybrid structure also demonstrated enhanced electrochemical performance in applications as an anode material for lithium ion batteries [159].

CNT-based amperometric transducers

The use of surfactants to disrupt the strong Van der Waal attractive forces between CNTs and consequently improve their solubility, is seen throughout the literature. This methodology is preferred as it preserves the structure and properties of the CNTs much better than alternative approaches such as covalent modification [161] of the surface.

Although various polymers [162-164], DNA [165] and detergents [166] have all shown potential as surfactants in this process, to date, sodium dodecyl sulfate (SDS) has been the most widely used [167-171]. SDS has been used to prepare suitable homogeneous dispersions of CNTs for the preparation of thin films at the electrode interface [172, 173]. Comparison of different CNTs dispersing strategies have been investigated [162-164] and applied to the fabrication of numerous modified electrode based sensing probes [68, 136].

An additional application of CNTs is as nano-probes. Here, carbon nano-probes can be exploited as atomic force microscopy [174, 175] or scanning tunnelling microscope [176, 177] tips.

CNT tips possess a number of advantages including:

- intrinsically small diameters [178]
- high ratio aspects that allow them to probe deep crevices and trench structures
- ability to buckle elastically that limits the force applied by the atomic force microscope probe and reduce deformation and damage to biological and organic samples [174] and
- easily modified to create functional probes.

The use of functionalised nanotubes as atomic force microscope tips has opened up applications for molecular recognition and chemically sensitive imaging in chemistry and biology. Choi *et al.* reported significant improvements in CNT tip fabrication methods. This was achieved through implementation of an analogue control of the nano manipulation in

scanning electron microscopy, which has improved the accuracy of CNT mounting compared to their previous digital control system [178].

The authors intend to further investigate the capabilities of the CNT tips, through their optimisation for more challenging samples, including different materials and narrower trenches. TermehYousefi and co-workers demonstrated the ability of CNT-atomic force microscopic tips to probe the surface of an individual biological cell to potentially measure different properties of the cell. Significantly, the method demonstrated potential for the analysis of cancer cells as well as determining the physical interior properties of cells [174]. A study from Slattery *et al.* determined that modification of an atomic force microscopic tip with SWCNTs, such as those in figure 4, enhanced the stability and sensitivity during the collection lifetime of an image. The authors determined that the smaller tip diameters also created a greater peak force which allowed the collection of the subsurface current collection on conducting polymer samples. This meant that the SWCNT tips could be used to produce current voltage maps of the surface and for multiple measurements without compromising the SWCNT attachment; making the tip suitable for high bias atomic force microscopic applications [179].

CNT-based electrochemical DNA sensors

Since Palecek's discovery that DNA was electrochemically active, direct detection of DNA and its bases by electrochemical sensors [180], DNA based sensors (or genosensors) have been widely used in biomedical and environmental research in the detection of food and environmental pollutants, genetic diseases, and identification of viruses and bacteria [40]. The combination of CNTs with DNA has attracted significant attention as it contributes to the development of faster and more cost effective electrochemical DNA detection methods with improved sensitivity.

Owing to the ability of CNTs in forming π- π bonds between their conjugated π systems and nucleobases they are ideal candidates for use in DNA and RNA sensing. Moreover, due to the inherent electrical conductivity of CNTs, they amplify the DNA/RNA sensing signal. The inherent conductivity of CNTs is significant because methods of amplification such as addition of NPs or enzymes that promote electron transfer are normally required to strengthen the usually weak DNA/RNA sensing signal [142].

Gutierrez *et al.*, reported the use of MWCNT – modified glassy carbon electrodes for the detection and quantification of amino acids, albumin and glucose [181]. The authors observed that repeatable amperometric quantification of histidine, serine and cysteine was possible at low potentials for sub – micromolar concentrations. The probes were also capable of detecting glucose at a limit of 182 nM. Gutierrez *et al.* successfully demonstrated the probes application for the detection of carbohydrates in beverages and amino acids and albumin in pharmaceuticals.

Similarly, work by Li and Lee [182] improved the detection limit of a DNA sensing system by a factor of 2 (approx. 140 pM) and significantly reduced the fabrication time by incorporating functionalised MWCNTS in the sensing system. They also anticipated that this advance in the fabrication system may be applied to the further miniaturisation of biosensors. DNA immobilised CNTs are ideally achieved by covalently binding DNA on a solid surface via a single point attachment. Most of the applications of immobilised oligonucleotide are based on the hybridisation between the immobilised oligonucleotide and its complementary DNA sequence. Guo *et al.* outlined the fabrication of a simple 8-Hydroxy-2′-deoxyguanosine, 8-OHdG (a commonly identified biomarker for oxidative DNA damage) sensor that demonstrated excellent electrochemical response to the oxidation of 8-OHdG, see figure 5, section A, illustrates the enhanced response of the modified probe, while sections B & C illustrate the probes linear response at different pHs and scan rates respectively. The sensor had good sensitivity and repeatability with a detection limit of 1.88 $x10^{-8}$ M. The probe itself was based on the modification of an underlying glassy carbon electrode with MWCNTS [181].

Work by Fedorovskaya *et al.* [183] demonstrated the application of an array of vertically aligned MWCNTs electrically coupled with a conducting substrate as a hybrid electrode for RNA recognition in solution. The authors prepared the hybrid electrodes by non-covalent immobilisation of decaribonucleotide ($(pA)_{10}$) or its 5′-pyrene conjugate ($PyrpA(pA)_9$) on the MWCNTs. It was observed that the capacitance of the hybrid electrodes increased upon potential cycling in the presence of complementary target oligonucleotide. The hybrid electrodes selectivity was clearly demonstrated as only complementary target recognition resulted in the evolution of the electrode capacitance. Moreover, the author observed improved selectivity and stability of the electrode probe was observed when the 5′-pyrene conjugate ($PyrpA(pA)_9$) was used to prepare the hybrid electrode as it allowed the sensing interface to retain the probe-target oligonucleotide duplex on the MWCNT surface [183].

Ozsoz's group [182] described the development of a MWCNT-modified genosensor for the detection of *Escherichia coli*. The authors reported that the modified electrodes promoted enhanced adsorption of the DNA probe, on the electrode sensing interface. This has resulted in a threefold signal enhancement and lower detection limit (17 nM) compared to a corresponding un-modified sensor. As the DNA probe was selectively sequenced for the target analyte eliminating the necessity for an additional bio label and thus, simplifying the sensing procedure significantly by removing the use of a mediator and the need for extra experimental steps for indicator-DNA interaction.

Zhang also reported the facile and efficient fabrication of a label-free impedimetric genosensor using CNTs functionalised with the Fe_3O_4 nanoparticles as the probe supporting substrate [184]. Zhang detailed that the Fe_3O_4/CNT nanocomposite membrane provided a large surface area with ideal biocompatibility for the probes DNA immobilisation. This method produced a highly sensitive (detection limit of 2.1 x 10^{-16} $molL^{-1}$) biosensor for the detection of the Breakpoint Cluster Region protein / ABelson murine Leukaemia viral oncogene homolog 1 (BCR/ABL) fusion gene in chronic myelogenous leukaemia. Moreover, Zhang outlined the exceptional selectivity of the biosensor with successful discrimination of the target DNA from other sequences. Finally, the author highlighted that the probe did not involve a complicated fabrication procedure and the strategy employed could easily be adapted for the facile fabrication of other DNA electrochemical bio – sensing platforms [184].

Liu and co – workers, outlined the development of a highly sensitive (possessing a limit of detection of 1 x 10^{-16} M) and specific electrochemical sensing system for the detection of the pathogenic bacteria *Clostridium tetani*, responsible for tetanus, that was dependent solely on two nanophase materials: gold nanoparticles and MWCNTs. Liu highlighted that the electrochemical sensor was an ideal and rapid method for the early diagnosis of tetanus, broadening the use of the DNA amplification method and holding great promise for future ultrasensitive bioassay applications [185] Figure 6 below, illustrates the impact of the gold nanoparticle functionalisation on the sensor's MWCNT morphology (A & B) and ultimately it sensitivity to the target analyte (D).

CNT-based gas sensors

The need for sensing gases arises from many applications in multiple fields including industrial, environmental and medical analyses. Conventionally, qualitative and quantitative

gas detection has been achieved via bulky instrumentation. An ideal alternative to these conventional methods is to use small scale sensors as they are considerably less expensive. However, their performance in the field must match that of established analytical instruments in order to gain acceptance. Therefore, nanomaterials as the sensing media/interface offer distinct advantages in their sensitivity and selectivity.

Work by Li *et al.* [186] systematically investigated the sensing mechanisms of multiple CNT – based devices for the detection of NH_3 and NO_2. The authors determined that the interaction between the molecule and the CNTs at the metal – CNT contact was the dominant sensing mechanism at low analyte concentrations. The authors noted that both ammonia and nitrogen dioxide can physisorb to a pristine CNT but adsorption only resulted in small current changes through the device. It was also observed that if a CNT is attached to a gold nanowire lead, the most sensitive detection site was at the CNT near the CNT-Au contact, where chemisorption occurs. The resulting change in electron transfer and low-bias current led to a 30 % increase in the sensitivity of the sensor.

Dhall and Jaggi reported an efficient procedure for the fabrication of two CNT hybrid composites for the detection of hydrogen gas. The authors exploited Raman and X-ray diffraction analysis to confirm the formation of hybrid composites. The results indicated that a nickel oxide functionalised – platinum decorated MWCNTs was more sensitive when compared to a cuprous oxide – functionalised – platinum decorated MWCNTs hybrid composite producing double the signal response for 0.05% H_2 gas at 25 ^{o}C [187].

Work from Kim and co – workers [188] detailed the fabrication of a p-channel field-effect transistor -type NO_x gas sensor using MWCNTs, a gold electrode was deposited on to a MWCNT film coated on to a p-type silicon wafer. The fabricated sensor proved useful for the detection of NO_x gas at various gate-source voltages. Although the authors observed that the decreased resistivity of the gas sensor as a function of absorbed NO_x could be countered by increasing the electrode spacing of the sensor.

In a study by Cismaru *et al.* [189] the design of a new type of radio frequency gas sensor based on an electromagnetic band cap resonator with couple-line structure in the centre area, covered by an MWCNT's transducer layer for the detection of methane. The characteristic interaction between methane molecules and CNTs was enhanced by the coupled waveguides which resulted in a high value of sensitivity, ten times greater than that observed for a sensor

unmodified by MWCNTs. Moreover, the frequency downshift was a further proof of the effect of methane on CNTs, i.e., an increase in resistance due to a decrease in the number of holes in the CNT electronic structure. The results presented, together with the compact dimensions of the device, clearly demonstrate the capabilities of CNTs in RF applications for sensing purposes [189].

Asad *et al.* [190] described the development of wearable Copper-SWCNTs-based sensors that exhibit enhanced response for hydrogen sulfide gas over a range of 5 ppm to 150 ppm. The authors demonstrated the rapid response time the sensor with a recovery time of 10 s to 15 s. The work also demonstrated the high selectivity of the sensor for the target gas, hydrogen sulfide, particularly in the presence of high concentrations of interfering gases. The authors report that the Copper-SWCNT modified polyethylene terephthalate flexible sensors were stable and offered reproducible responses at room temperature with the sensing performance remaining consistent over various bending radii. The authors hypothesised that the response observed was due to the Copper-SWCNT system strongly adsorbing hydrogen sulfide. The fabricated sensors were capable of real-time analysis of hydrogen sulfide with high sensitivities (concentrations as low as 5 ppm) and low power (1 V) consumption that enabled their integration with low power microelectronic circuits.

Zhang's group [191] reported the fabrication of a novel NO_2 sensor that exploits reduced graphene oxide-CNT-SnO_2 hybrids as the sensing element. These were prepared by hydrothermal treatment of graphene oxide-CNT in the presence of tin (IV) chloride. The sensors displayed high sensitivity (5 ppm NO_2), rapid response (8 compared to the 135 seconds reported previously [192]) and fast recovery rate (77 compared to 200 seconds to return to baseline). Enhanced selectivity and response stability for NO_2 at room temperature was also achieved in comparison to previously reported reduced graphene oxide -based NO_2 sensors [191].

Abudulla *et al.* [193] reported the development of a polyaniline functionalised multiwalled carbon nanotubes (PANI/MWCNTs) based nanocomposite for the detection of trace levels of ammonia (NH_3) gas. The authors outline the PANI/MWCNT nanocomposite based sensors improved sensor response (15.5 % versus 2.58%) and response/recovery characteristics (response time of 6 s rather than 965 s and a recovery time of 35 s rather than 1140 s) in comparison to an un-functionalised probe.

Flexible electronics have multiple potential applications including integrated electronic devices and wearable sensors. At present a large area of research had focused on improving such devices robustness with an emphasis on their flexibility, particularly its reliability. Inspired by the natural world, researchers are attempting to mimic the "healability" of multiple organisms. Moreover, to further appeal to industry researchers are striving to develop transparent materials that can be affixed to products such as clothing without impacting its appearance. Bai *et al.* [194], report the development of a flexible "healable" transparent chemical gas sensor device assembled from a functionalised with oxygenated functional groups, such as carbonyl, hydroxyl and epoxy groups MWCNTs network-coated polyelectrolyte multilayer film. The authors described how the layer by layer assembled polyelectrolyte multilayer films successfully imparted "healability" to the functionalised MWCNT network layer by the lateral movement of the underlying healable layer, bringing the separated areas of the MWCNT layer back into contact in the presence of water. The authors detail how the sensor may be cut and restored multiple times with a small (2 %) drop in the sensors performance after several cycles. It was shown that with the superior CNT network structures being anchored on self-healing substrates, that the sensor exhibited robust flexibility, good transparency, and reliable water-enabled "healability" and was capable of gas sensing performance at room temperature. This work demonstrated the potential to develop healable transparent nano – electronics with the exciting benefits of reduced raw material consumption, decreased maintenance costs, improved lifetime, and robust functional reliability [194].

In their work Piloto and co – workers [195] demonstrated the scalable fabrication of ultrathin CNT conductometric sensors that operate at room temperature in a surfactant-free process. This is a benefit as the majority of CNT fabrication process are not scalable or depend on CNT surfactant based dispersions, the surfactants are often difficult to remove and can cause issues in their later applications. The films were robust, thin and could be integrated into flexible and transparent electronic applications. The sensor performed well at low concentrations, exhibiting limits of detection of 1 ppm for NO_2 and 7 ppm for NH_3. The authors attributed the high sensitivity to the high density of CNTs deposited in an ultrathin film (~ 5 nm) by dip coating. Further improvements in the sensing performance were achieved via sonication of the CNTs film. The authors hypothesised that the CNT films can be used as sensing layer for the development of inexpensive, high performance room temperature gas sensors.

Finally, Humayun *et al.*, [196] reported the fabrication of chemoresistive sensors based on SnO_2 nanocrystal functionalised MWCNTs for detecting CH_4 gas with 10 ppm limit of detection. The authors stated that the sensors sensitivity even for trace analytes, (single ppm level),coupled with its significant reversible relative resistance change, was directly related to the extent of successful functionalisation of the MWCNT surface by the SnO_2 nanocrystals, as no response was observed for CH_4 by un-functionalised MWCNT based probes.

Electrochemistry has always provided analytical techniques characterised by instrumental simplicity, moderate cost and portability [197]. The application of diamond surfaces as an electrochemical sensing interfaces has rapidly increased in recent years with the advent of improved fabrication and modification techniques. Here we discuss diamonds the effectiveness of diamond as a substrate for an electrochemical sensor and its application as a probe for numerous analytes.

Boron-doped diamond (Characterisation of diamond surfaces)

The ratio of sp^2/sp^3 carbon is often an indicator for diamond purity, and Raman spectroscopy is the traditional technique for estimating this ratio [198]. In a recent work, the sp^2 content of carbon sites was determined using boron-doped diamond electrodes to examine the electroactive quinone groups present [199]. The sp^2 content of is generally associated with the provision of pH active functional groups and enhanced electrocatalytic properties. Ayres *et al.* also noted that this technique was sensitive enough to detect quinone groups even on electrodes which had low sp^2 content, observing quinone signal demonstrated a 3 × signal to noise ratio. The authors were also able to distinguish between four different electrodes and place them in order of increasing sp^2 surface content and proposed quinone surface coverage measurements as an alternative method to Raman microscopy.

Metronidazole

Metronidazole is a substituted imidazole antibiotic widely used to treat anaerobic bacterial infection caused by *Helicobacter pylori*, and *protozoal* infections [200]. Amar *et al.,* [201] conducted cyclic voltammetry and square wave voltammetry of metronidazole at a boron–doped diamond electrode in an aqueous medium. For comparison, performances of a silver electrode and a glassy carbon electrode were also studied. In cyclic voltammetric

experiments, Ammar reported an irreversible cathodic peak corresponding to the nitro group in metronidazole, with the maximum current obtained using the boron-doped diamond electrode. In addition, a limit of detection of 65 nmol L^{-1} was obtained.

Ziram

In another study, Stankovic *et al.* reported the amperometric detection of the pesticide ziram using boron-doped diamond electrodes. The working electrode was embedded in a polyether ether ketone body with an inner diameter of 3 mm, and was characterised to possess a resistivity of 0.075 Ω cm and a boron doping level of 1000 ppm. A wide linear range from 10 to 1000 nM was obtained with an estimated limit of detection of 2.7 nM at the electrode, and replicative experiments showed a standard deviation of less than 3 %. The proposed method was successfully applied for ziram quantification in spiked river water samples [202].

Oxalic acid

Watanabe *et al.* [203] reported the development of a prototype microfluidic device using boron-doped diamond electrodes patterned on alumina chips. The device was utilised to analyse the oxalic acid content in vegetables. Detection of this compound in biological materials is desirable, because it acts as an anti – nutrient, as a toxin, and in the formation of calcium oxalate which gives rise to kidney stones. As the oxalate di – anion ($C_2O_4^{2-}$) is oxidised at a high positive potential; it can be electrochemically detected using a boron-doped diamond electrode, which was otherwise demonstrated to be difficult using conventional electrodes such as glassy carbon electrodes [204]. This is a consequence of boron-doped diamond electrodes superior resistance to fouling, a product of their compact sp^3 configuration, in comparison to the porous sp^2 structure of glassy carbon. The authors reported that flow injection analysis of oxalic acid at the fabricated device was successful and that electrochemical conditioning steps without changing the solution were effective for obtaining reliable and reproducible signals. Furthermore, the high durability of boron-doped diamond allowed its application in robust treatments not only for conditioning but also as a measure against fouling.

Imatinib

Boron-doped diamond has also been applied to an electroactive probe surface by Brycht *et al.* to detect the anticancer drug, imatinib on a voltammetric platform [205]. Cyclic voltammetry of imatinib at the electrode displayed an electrochemical irreversible response. The sensor was found to demonstrate irreversible and exclusive (in the absence of imatinib no redox peaks were observed over the entire working potential range) oxidation of imatinib which is an advantageous trait for trials in the *in vivo* space. A limit of detection of 6.3 nmol L^{-1} for imatinib was estimated.

7-methylguanine

Another biologically-derived entity, 7-methylguanine, is of interest to analysts due to its possible association with cancerous tumours [206]. Recent work by Sanjuán *et al.* has developed two detection schemes for 7-methylguanine. The first was a polycrystalline boron-doped diamond film mounted in polyether ether ketone doped with a 0.1% of boron as the working electrode and its performance was compared with that of a glassy carbon electrode. The second electrochemical configuration used a 50 μL working solution drop on a screen-printed graphite electrode where the 3.0 mm diameter graphitic working surface of the screen printed electrode served as the counter electrode and the Ag|AgCl pseudo reference acted as the reference electrode. This electrode scheme is depicted in Figure 7.

The authors found that a ~50 % lower capacitive current and better defined oxidative peak features for 7-methylguanine were achieved at the boron –doped diamond electrodes relative to a glassy carbon electrode. Electrode selectivity in the presence of guanine and adenosine, which are known interfering species in the voltammetric determination of 7-methylguanine [208] was also evaluated. Separations of 120 mV and 300 mV were observed between peaks attributed to guanine and adenosine and 7-methylguanine, respectively [207]. Furthermore, calibration plots for 7-methylguanine were found to be linear in the range of 10 – 200 μM, with regression ($R^2 = 0.997$) and a sensitivity of 0.0332 μA μM^{-1}. Sanjuán and colleagues also identified the potential for applying the boron-doped diamond electrodes as sensing devices for 7-methylguanine in biological samples (DNA by extraction or other biological fluids, such as urine), which can serve as a biomarker for the detection of abnormal methylation patterns [207].

Uric acid, ascorbic acid and dopamine

Dopamine is a major neurotransmitter involved in initiating many behavioural responses to various stimuli, and it also plays a crucial role in the functioning of the central nervous, cardiovascular, renal, and hormonal systems, as well as emotional and reward processes [209]. Uric acid is the final oxidation product of purine metabolism and exists in biological fluids such as blood or urine. Disorders of uric acid are symptoms of several diseases such as gout and hyperuricemia [210]. Therefore, there is considerable research input into sensitive and selective detection of both species in the physiological space. To this end, nitrogen-incorporated ultrananocrystalline diamond electrodes have been the focus of interest and were evaluated in the electrochemical detection of uric acid and dopamine by Skoog *et al.* [211].

The authors conducted linear scan voltammetry of uric acid and dopamine *in vitro* from 0.2 V to 0.8 V at 10 mV/s. Uric acid concentrations varying from 0 to 200 μM were evaluated and a distinct oxidation peak was observed at a potential of 0.48 V as well as a linear relationship between the uric acid concentration and the peak current throughout the detection range. Dopamine concentrations were detected in a linear concentration range from 0 to 30 μM at an oxidation peak potential of 0.65 V. Importantly, the oxidative peaks between the two analytes were separated by ~ 200 mV when tested separately. However, attempts to detect the two analytes simultaneously were unsuccessful and only a single peak was observed due to overlapping of the individual signals [211]. Other researchers have also previously alluded to this overlap and obtained satisfactory resolution during simultaneous detection of dopamine and uric acids at nitrogen-doped diamond electrodes. For example, Shalini *et al.* demonstrated simultaneous detection of dopamine, uric acid, and ascorbic acid with significant peak separation using nitrogen-doped diamond electrodes [212, 213]. They noted that the nitrogen-doped diamond electrodes demonstrated superior peak separation compared to others such as boron-doped diamond, graphite, and glassy carbon electrodes and hypothesised that this was due to the electrodes sp^2 graphitic phase and the nanowire-like structure, a consequence of the incorporation of N_2 in the growth plasma of the diamond electrodes. The authors also suggested that nitrogen-incorporated ultrananocrystalline diamond microneedle-based device may serve as an attractive platform for minimally invasive, continuous monitoring of physiologically relevant molecules [211].

Boron-doped diamond electrodes have also been applied towards the detection of dopamine and ascorbate. The simultaneous detection of both species using glassy carbon electrodes is

well known to be constrained by the similar oxidation potentials of both, as well as the larger concentration of ascorbate compared to that of dopamine in the brain where both are encountered. Furthermore, the oxidised product of dopamine, dopamine quinone, is reduced back to dopamine by ascorbate, thus giving rise to an amplified dopamine oxidation signal in the presence of ascorbate [214]. To be able to resolve the overlapping signals between both ascorbate and dopamine represents significant research gains in developing probes for *in vivo* dopamine/ascorbic acid detection. To this end, Qi *et al.* have prepared boron-doped diamond with different thickness using hot filament chemical vapour deposition and evaluated their performance in detecting dopamine and ascorbate. Cyclic voltammetry of both species performed at the electrodes showed a clear peak potential difference on 8 h- and 12 h-deposited electrodes, indicating that the thickness of electrodes exhibited a strong impact on the resolution of dopamine/ascorbate oxidation peaks. Additionally, a limit of detection of 1 μM dopamine in the presence of 1 mM ascorbic acid was the lowest at the 12 h-deposited boron-doped diamond electrode [215].

Yang and co-workers have compared the electrochemical properties and biosensing performance of nanodiamond-derived carbon nano-onions with three commonly used carbon materials: MWCNTs, graphene nanoflakes and glassy carbon [216]. Carbon nano-onions are spherical, closed carbon shells similar to the concentric layered structure of an onion. They are also often referred to as carbon onions or onion-like carbon. Those names cover all kinds of concentric shells, from nested fullerenes to small (<100 nm) polyhedral nanostructures [217]. Yang *et al.* reported the simultaneous detection of ascorbate, dopamine and uric acid at a nickel modified boron-doped diamond electrode by differential voltammetric measurements. The nanodiamond-derived carbon nano-onions demonstrated a superior sensitivity for dopamine detection over the MWCNTs. Moreover, nanodiamond-derived carbon nano-onions exhibited nearly 6× larger current density arising from dopamine oxidation than MWNCTs, along with sufficient peak separations of all three analytes (peak separations of ascorbate–dopamine and dopamine–uric acid were 274 mV and 122 mV, respectively). Overall, nanodiamond-derived carbon nano-onions showed excellent electrocatalytic activities with fast electron transfer kinetics and large oxidation current densities, thus revealing a great potential for the detection of redox-active biomolecules with ultra-high sensitivity at the material [216].

In a recent work, Peltola *et al.* [218], have combined tetrahedral amorphous carbon with nanodiamonds to provide a new platform for biosensor applications. The electrodes were

subjected to cyclic voltammetry in various concentrations of dopamine in the presence of 1 mM ascorbic acid in phosphate buffered saline and rinsed in the same buffer between measurements. Performance evaluation of the electrodes showed hydroxyl functionalised nanodiamond showed the lowest detection limit (50 nM) for dopamine, followed by nanodiamond modified with a mixture of amine and hydroxyl groups and amine functionalised nanodiamond (100 nM). The dopamine detection limit for carboxyl functionalised nanodiamond was an order of magnitude higher (500 nM) than for hydroxyl modified nanodiamond. All the electrodes showed a broad linear range for dopamine detection: amine and hydroxyl functionalised nanodiamond 100 nM^{-1} mM, amine modified nanodiamond 100 nM – 1 mM, carboxyl functionalised nanodiamond 500 nM – 100 μM, and hydroxyl functionalised nanodiamond 50 nM – 1 mM. Sensitivities of the drop-casted electrodes were 0.195 – 0.248 A M^{-1} cm^{-2}. Overall, the authors concluded that by using nanodiamonds on tetrahedral amorphous thin films, sensitivity towards dopamine could be improved.

Glucose

Most glucose sensors are based on the classic Clark's experiment of glucose oxidase-glucose coupling at a sensor interface [219]. However, in recent times, various types of electrodes have been employed in such analysis particularly in biosensing where the problem associated with the transient decay of enzyme activity or pH- and temperature-related disruptions have been mitigated with the development of enzyme-less sensors [220, 221]. Readers are referred to the several publications devoted to enzymeless glucose detection, such as those of Scognamiglio *et al.*[222], Hasan *et al.* [223] and Carbone *et al.* [224].

Recently, Deng *et al.*, have reported developing a nickel-microcrystalline graphite-boron doped diamond electrode for detecting glucose in vitro [225].The electrode determines the concentration of glucose via it's oxidation to gluconolactone. The electrocatalytic activity of the nickel-based electrodes for glucose oxidation is associated with the formation of nickel oxide hydroxide layer at the electrodes surface. Deng observed that the electrode exhibited two linear dependence of current responses with glucose concentration ranges from 0.002 – 0.5 and 0.5 – 15.5 mM with a high sensitivity of 1010.8 and 660.8 μA mM^{-1} cm^{-2}, respectively. The electrode also exhibited a low detection limit of 0.24 μM (S/N = 3), good

selectivity and reproducibility, and excellent stability during the long-term electrochemical detection [225].

A stable and sensitive non-enzymatic glucose sensor prepared by modifying a boron-doped diamond electrode with nickel nanosheets and nanodiamonds has been reported by Dai and co-workers [216]. The electrode exhibited a stable, fast response, with two concentration ranges (similar to that of Deng *et al.*, above); 0.2 – 12 and 31.3 – 1055.4 μM with a sensitivity of 20 μA mM^{-1} cm^{-2} and 35.6 μA mM^{-1} cm^{-2}, respectively. The detection limit was estimated to be 0.05 μM (S/N = 3). The authors have attributed the lower sensitivity to the adsorption of intermediates from the oxidation of glucose (gluconolactone and sodium gluconate in a 0.1 M NaOH electrolyte), and the slower adsorption of glucose at higher concentration. Notably, the authors also applied the electrodes to human serum samples, where the recovery values of glucose obtained by standard additions of glucose to the serum samples ranged from 96.1% to 103.1%, confirming that the sensor could be used practically for routine analysis of glucose in real-life biological samples [216].

Environmental analysis

Hybrid diamond/graphite nanostructures for electrochemical applications have been synthesised using microwave plasma enhanced chemical vapour deposition by Guo and co-workers [181]. During the electrochemical study, a conductive hybrid diamond/graphite film was used as working electrode. Guo reported quasi-reversible behaviour at the electrode surface, mass controlled electrode reactions in aqueous and organic solutions and a wide potential window of about 3.1 V. Moreover, the electrode enabled low detection limits of 5.8 ppb for Ag^{+} and 5.6 ppb for Cu^{2+}, respectively. The good recovery values in tap water samples demonstrate the accuracy and feasibility of the hybrid diamond/graphite electrodes. The hybrid diamond/graphite electrode is thus a potential candidate for trace heavy metal ions detection.

Phenol has been found in various sources including industrial effluents, coal gasification, pesticide production, fertilisers, dyes, and other chemicals. Despite it being biodegradable, the presence of phenol can be growth inhibitory to microorganisms at elevated concentrations [226] thus, its screening and quantification are important. Ajeel *et al.* [227] have developed

carbon black diamond composite electrodes for anodic degradation of phenol with the removal efficiency for phenol reported of more than 97% after 27 hours at pH 3.

Very recent work by Hébert and co-workers has seen the development of a hybrid of the porous, conductive polymer of polypyrrole and diamond to yield a material with high double layer capacitance, low interfacial impedance, high charge storage capacitance, high resistance to corrosion and high biocompatibility [228]. The material was found to yield a double layer capacitance as high as 3 mF cm^{-2} and an electrochemical impedance typically 600 times lower than that an of un-functionalised diamond electrode in aqueous $LiClO_4$. [229].

Biosensors

Lactate levels in clinical practice are often used as a surrogate for illness and to gauge response to therapeutic interventions [230]. Tissue hypoxia or oxygen debt that cause high lactate levels in a person can often be a result of sepsis, shock, heart attack/failure, organ failure or diabetes. For these important reasons, lactate determination is a routine parameter in clinical evaluations, often through blood-gas analysers as the conventional route for lactate determinations, despite emerging strip-based technology [231]. Recently, the modification of a gold electrode with un-doped diamond nanoparticles to constitute a sensor and its applicability to the application of lactate was evaluated and reported [232]. Briones concluded that the sensor showed clear electrocatalytic responses towards lactate, demonstrating a linear concentration range from 0.05 mM to 0.7 mM, a sensitivity of 4.0 μA/mM, a detection limit of 15 μM and a good reproducibility (RSD 6%). Thus compared with commercial strip methods that yield limits of detection of 0.21, 0.30 and 20 mg/L, the lactate sensor achieved a reasonable limit of detection.

Cochlear implants have been used for several decades to treat patients with profound hearing loss [233]. Despite this, cochlear implants provide only a very crude mimicking of only some aspects of the normal physiology [234]. A major problem is the delivery of independent stimulation signals to individual auditory neurons. Fine hearing requires significantly more stimulation contacts with intimate neuron/electrode interphases from ordered axonal re-growth, something current technology cannot provide.

Cai *et al.* have explored the potential application of micro – textured nano – crystalline diamond surfaces on cochlear implant electrode arrays. The authors concluded that

regenerating auditory neurons showed a strong affinity to the nano – crystalline diamond pillars, and the technique could be used for neural guidance and the creation of new neural networks. Together with the unique anti-bacterial and electrical properties of nano – crystalline diamond, patterned surfaces could provide designed neural/electrode interfaces to generate independent electrical stimulation signals in cochlear implant electrode arrays for the neural population [186].

Zhang *et al.*, have used a simple approach of low-power sonication-assisted seeding technique to fabricate a bio – functionalised nanodiamond -seeded interdigitated electrode for label-free pathogen detection [235]. Their findings showed that higher surface coverages were important for improved bacterial capture and could be achieved through proper choice of solvent, nanodiamond concentration, and seeding time. Based on electrochemical impedance spectroscopy of phosphate buffer solutions over a range of conductivities (737 μScm^{-1} – 16500 μScm^{-1}) at these nanodiamond-seeded interdigitated electrodes, the nanodiamond seeds were found to serve as electrically conductive islands only a few nanometers apart. When sensing bacteria from 10^6 CFU/mL *E. coli O157:H7*, the charge transfer resistance at the interdigitated electrodes decreased by ~38.8% which was nearly 1.5× better than that reported previously using redox probes. Further in the case of 10^8 cfu/mL *E. coli O157:H7*, the charge transfer resistance decreased by ~46%, which was similar to the magnitude of improvement reported using magnetic nanoparticle-based sample enrichment prior to impedance detection. Thus, the authors concluded nanodiamond seeding allowed impedance biosensing in low conductivity solutions with competitive sensitivity [235].

Conclusion

The unique properties of carbon nanomaterials have extensively contributed to the development and evolution of electrochemical sensors and biosensors. Both the novel and modified carbon based probes often display enhanced analytical performance with respect to conventional non- nanostructured electrochemical systems.

Electroanalytical methods using sensing and biosensing devices involving carbon nanostructure modified electrodes are showing promise for application to real-life analytical detection. In particular CNTs and diamond have been exploited as electrode materials for electrochemical sensing for a myriad of analytes. The unique properties of CNTs, diamond

and diamond – like films have extensively contributed to the design of novel nanostructured electrochemical sensors and biosensors, with enhanced analytical performance compared to traditional electrochemical sensing systems. Although some challenges still remain, for example, reproducibility and scalability of current "nano" devices, the sensing systems are very much affected by the properties of the nanostructures used, (e.g. diameter and the chirality of SWCNTS). Furthermore, more appropriate estimations of some performance characteristics and their application for sensing analytes in real – world samples are necessary before potential commercialisation.

The impact of carbon nanomaterials in modern electrochemical systems is supported by the superior performance analytically, coupled with their novel properties such as the electrocatalytic ability of carbon nanomaterial modified electrodes, such as the enhanced active surface area of CNTs and the anti-fouling capability of diamond and diamond like surfaces.

Moreover, as new, tuneable methodologies for the synthesis and functionalisation of carbon nanomaterial continue to be developed, the authors envision that this will result in a rising number of important electroanalytical applications in the near future in multiple fields of interest, such as rapid and sensitive medical analyses, drug quality monitoring, food and environment security.

The authors also anticipate that a large portion of future efforts will focused on the development of bioinspired new hybrid carbon sensors that are capable of being processed on flexible substrates. The overall progress of this research field will have enormous implications for both fundamental scientific discovery and technological development. The potential sensors could be used to study electron transfer in naturally occurring biomolecules. Particularly as such an investigation of the interface of biology and electronics could lead to the fabrication of novel portable devices for use in advancing both human health and environmental monitoring globally.

References

[1] F.W. Campbell and R.G. Compton, *The use of nanoparticles in electroanalysis: an updated review.* Analytical and bioanalytical chemistry, 2010. **396**(1): p. 241-259.

[2] J.C. Ndamanisha and L.-p. Guo, *Ordered mesoporous carbon for electrochemical sensing: a review.* Analytica chimica acta, 2012. **747**: p. 19-28.

[3] O. Amor-Gutiérrez, E.C. Rama, A. Costa-García, and M. Fernández-Abedul, *Paper-based maskless enzymatic sensor for glucose determination combining ink and wire electrodes.* Biosensors and Bioelectronics, 2016.

[4] L. Fu, Y. Zheng, and A. Wang, *Poly (diallyldimethylammonium chloride) functionalized reduced graphene oxide based electrochemical sensing platform for luteolin determination.* Int J Electrochem Sci, 2015. **10**: p. 3518-3529.

[5] L. Nyholm, *Electrochemical techniques for lab-on-a-chip applications.* Analyst, 2005. **130**(5): p. 599-605.

[6] A. Rahi, K. Karimian, and H. Heli, *Nanostructured materials in electroanalysis of pharmaceuticals.* Analytical biochemistry, 2016. **497**: p. 39-47.

[7] N. Yang, G.M. Swain, and X. Jiang, *Nanocarbon electrochemistry and electroanalysis: current status and future perspectives.* Electroanalysis, 2016. **28**(1): p. 27-34.

[8] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, *C 60: buckminsterfullerene.* Nature, 1985. **318**(6042): p. 162-163.

[9] S. Iijima, *Helical microtubules of graphitic carbon.* nature, 1991. **354**(6348): p. 56.

[10] M.F. De Volder, S.H. Tawfick, R.H. Baughman, and A.J. Hart, *Carbon nanotubes: present and future commercial applications.* Science, 2013. **339**(6119): p. 535-539.

[11] X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo, and X. Bao, *Enhanced ethanol production inside carbon-nanotube reactors containing catalytic particles.* Nature materials, 2007. **6**(7): p. 507-511.

[12] M. Prato, K. Kostarelos, and A. Bianco, *Functionalized carbon nanotubes in drug design and discovery.* Accounts of chemical research, 2007. **41**(1): p. 60-68.

[13] M. Trojanowicz, *Analytical applications of carbon nanotubes: a review.* TrAC trends in analytical chemistry, 2006. **25**(5): p. 480-489.

[14] R. Dastjerdi and M. Montazer, *A review on the application of inorganic nano-structured materials in the modification of textiles: focus on anti-microbial properties.* Colloids and Surfaces B: Biointerfaces, 2010. **79**(1): p. 5-18.

[15] D.S. Hecht, L. Hu, and G. Irvin, *Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures.* Advanced Materials, 2011. **23**(13): p. 1482-1513.

[16] S. Iijima, *Carbon nanotubes: past, present, and future.* Physica B: Condensed Matter, 2002. **323**(1): p. 1-5.

[17] S. Iijima and T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter.* Nature, 1993. **363**(6430): p. 603-605.

[18] A. Qureshi, W.P. Kang, J.L. Davidson, and Y. Gurbuz, *Review on carbon-derived, solid-state, micro and nano sensors for electrochemical sensing applications.* Diamond and Related Materials, 2009. **18**(12): p. 1401-1420.

[19] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation.* Nature nanotechnology, 2006. **1**(1): p. 60-65.

[20] Ş. Erkoç, *Structural and Electronic Properties of Carbon Nanotubes.* International Journal of Modern Physics C, 2000. **11**(01): p. 175-182.

[21] T.W. Odom, J.-L. Huang, P. Kim, and C.M. Lieber, *Atomic structure and electronic properties of single-walled carbon nanotubes.* Nature, 1998. **391**(6662): p. 62-64.

[22] T.W. Odom, J.-L. Huang, P. Kim, and C.M. Lieber, *Structure and electronic properties of carbon nanotubes*. 2000, ACS Publications.

[23] Q. Cao, S.-j. Han, G.S. Tulevski, Y. Zhu, D.D. Lu, and W. Haensch, *Arrays of single-walled carbon nanotubes with full surface coverage for high-performance electronics.* Nature Nanotechnology, 2013. **8**(3): p. 180-186.

[24] J.E. Fischer and A.T. Johnson, *Electronic properties of carbon nanotubes.* Current Opinion in Solid State and Materials Science, 1999. **4**(1): p. 28-33.

[25] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, and M.C. Hersam, *Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing.* Chemical Society Reviews, 2013. **42**(7): p. 2824-2860.

[26] U.N. Maiti, W.J. Lee, J.M. Lee, Y. Oh, J.Y. Kim, J.E. Kim, J. Shim, T.H. Han, and S.O. Kim, *25th anniversary article: chemically modified/doped carbon nanotubes & graphene for optimized nanostructures & nanodevices.* Advanced materials, 2014. **26**(1): p. 40-67.

[27] Q. Zhang, E. Uchaker, S.L. Candelaria, and G. Cao, *Nanomaterials for energy conversion and storage.* Chemical Society Reviews, 2013. **42**(7): p. 3127-3171.

[28] E. Akbari, Z. Buntat, M.H. Ahmad, A. Enzevaee, R. Yousof, S.M.Z. Iqbal, M.T. Ahmadi, M.A.B. Sidik, and H. Karimi, *Analytical calculation of sensing parameters on carbon nanotube based gas sensors.* Sensors, 2014. **14**(3): p. 5502-5515.

[29] K. Ali and M. Hafez, *Growth and structure of carbon nanotubes based novel catalyst for ultrafast nano-temperature sensor application.* Superlattices and Microstructures, 2013. **54**: p. 1-6.

[30] F. Lorestani, Z. Shahnavaz, P. Mn, Y. Alias, and N.S. Manan, *One-step hydrothermal green synthesis of silver nanoparticle-carbon nanotube reduced-graphene oxide composite and its application as hydrogen peroxide sensor.* Sensors and Actuators B: Chemical, 2015. **208**: p. 389-398.

[31] H.-L. Lu, C.-J. Lu, W.-C. Tian, and H.-J. Sheen, *A vapor response mechanism study of surface-modified single-walled carbon nanotubes coated chemiresistors and quartz crystal microbalance sensor arrays.* Talanta, 2015. **131**: p. 467-474.

[32] A. Misra, *Carbon nanotubes and graphene-based chemical sensors.* Current Science, 2014. **107**(3): p. 419-429.

[33] H.T. Chung, J.H. Won, and P. Zelenay, *Active and stable carbon nanotube/nanoparticle composite electrocatalyst for oxygen reduction.* Nature communications, 2013. **4**: p. 1922.

[34] D.S. Su, S. Perathoner, and G. Centi, *Nanocarbons for the development of advanced catalysts.* Chemical reviews, 2013. **113**(8): p. 5782-5816.

[35] W. Yuan, S. Lu, Y. Xiang, and S.P. Jiang, *Pt-based nanoparticles on non-covalent functionalized carbon nanotubes as effective electrocatalysts for proton exchange membrane fuel cells.* Rsc Advances, 2014. **4**(86): p. 46265-46284.

[36] Y. Zhai, Z. Zhu, and S. Dong, *Carbon‐Based Nanostructures for Advanced Catalysis.* ChemCatChem, 2015. **7**(18): p. 2806-2815.

[37] D.-W. Wang and D. Su, *Heterogeneous nanocarbon materials for oxygen reduction reaction.* Energy & Environmental Science, 2014. **7**(2): p. 576-591.

[38] A. Kamyshny and S. Magdassi, *Conductive nanomaterials for printed electronics.* Small, 2014. **10**(17): p. 3515-3535.

[39] S. Park, M. Vosguerichian, and Z. Bao, *A review of fabrication and applications of carbon nanotube film-based flexible electronics.* Nanoscale, 2013. **5**(5): p. 1727-1752.

[40] C. Yang, M.E. Denno, P. Pyakurel, and B.J. Venton, *Recent trends in carbon nanomaterial-based electrochemical sensors for biomolecules: A review.* Analytica chimica acta, 2015. **887**: p. 17-37.

[41] R. Marega, F. De Leo, F. Pineux, J. Sgrignani, A. Magistrato, A.D. Naik, Y. Garcia, L. Flamant, C. Michiels, and D. Bonifazi, *Functionalized Fe‐Filled Multiwalled Carbon Nanotubes as Multifunctional Scaffolds for Magnetization of Cancer Cells.* Advanced Functional Materials, 2013. **23**(25): p. 3173-3184.

[42] G. Yu, W. Wu, Q. Zhao, X. Wei, and Q. Lu, *Efficient immobilization of acetylcholinesterase onto amino functionalized carbon nanotubes for the fabrication of high sensitive organophosphorus pesticides biosensors.* Biosensors and Bioelectronics, 2015. **68**: p. 288-294.

[43] T. Guinovart, M. Parrilla, G.A. Crespo, F.X. Rius, and F.J. Andrade, *Potentiometric sensors using cotton yarns, carbon nanotubes and polymeric membranes.* Analyst, 2013. **138**(18): p. 5208-5215.

[44] K. Rana, G. Kucukayan-Dogu, and E. Bengu, *Growth of vertically aligned carbon nanotubes over self-ordered nano-porous alumina films and their surface properties.* Applied Surface Science, 2012. **258**(18): p. 7112-7117.

[45] H. Zhang, G. Liu, and C. Chai, *A novel amperometric sensor based on screen-printed electrode modified with multi-walled carbon nanotubes and molecularly imprinted membrane for rapid determination of ractopamine in pig urine.* Sensors and Actuators B: Chemical, 2012. **168**: p. 103-110.

[46] Y. Zhao, L. Fan, B. Hong, J. Ren, M. Zhang, Q. Que, and J. Ji, *Nonenzymatic detection of glucose using three-dimensional PtNi nanoclusters electrodeposited on the multiwalled carbon nanotubes.* Sensors and Actuators B: Chemical, 2016. **231**: p. 800-810.

[47] G. Göbel, T. Dietz, and F. Lisdat, *Bienzyme sensor based on an oxygen reducing bilirubin oxidase electrode.* Electroanalysis, 2010. **22**(14): p. 1581-1585.

[48] N. Hernández-Ibáñez, L. García-Cruz, V. Montiel, C.W. Foster, C.E. Banks, and J. Iniesta, *Electrochemical lactate biosensor based upon chitosan/carbon nanotubes modified screen-printed graphite electrodes for the determination of lactate in embryonic cell cultures.* Biosensors and Bioelectronics, 2016. **77**: p. 1168-1174.

[49] A. Chen, D. Du, and Y. Lin, *Highly sensitive and selective immuno-capture/electrochemical assay of acetylcholinesterase activity in red blood cells: a biomarker of exposure to organophosphorus pesticides and nerve agents.* Environmental science & technology, 2012. **46**(3): p. 1828-1833.

[50] D. Futra, L.Y. Heng, M.Z. Jaapar, A. Ulianas, K. Saeedfar, and T.L. Ling, *A novel electrochemical sensor for 17β-estradiol from molecularly imprinted polymeric microspheres and multi-walled carbon nanotubes grafted with gold nanoparticles.* Analytical Methods, 2016. **8**(6): p. 1381-1389.

[51] C.-z. Li, H. Karadeniz, E. Canavar, and A. Erdem, *Electrochemical sensing of label free DNA hybridization related to breast cancer 1 gene at disposable sensor platforms modified with single walled carbon nanotubes.* Electrochimica Acta, 2012. **82**: p. 137-142.

[52] E.N. Primo, M.B. Oviedo, C.G. Sánchez, M.D. Rubianes, and G.A. Rivas, *Bioelectrochemical sensing of promethazine with bamboo-type multiwalled carbon nanotubes dispersed in calf-thymus double stranded DNA.* Bioelectrochemistry, 2014. **99**: p. 8-16.

[53] L. Bai, D. Wen, J. Yin, L. Deng, C. Zhu, and S. Dong, *Carbon nanotubes-ionic liquid nanocomposites sensing platform for NADH oxidation and oxygen, glucose detection in blood.* Talanta, 2012. **91**: p. 110-115.

[54] T.-Y. Huang, J.-H. Huang, H.-Y. Wei, K.-C. Ho, and C.-W. Chu, *rGO/SWCNT composites as novel electrode materials for electrochemical biosensing.* Biosensors and Bioelectronics, 2013. **43**: p. 173-179.

[55] H. Teymourian, A. Salimi, and R. Hallaj, *Low potential detection of NADH based on Fe_3O_4 nanoparticles/multiwalled carbon nanotubes composite: fabrication of integrated dehydrogenase-based lactate biosensor.* Biosensors and Bioelectronics, 2012. **33**(1): p. 60-68.

[56] Y. Lin, X. Chen, Y. Lin, Q. Zhou, and D. Tang, *Non-enzymatic sensing of hydrogen peroxide using a glassy carbon electrode modified with a nanocomposite made from carbon nanotubes and molybdenum disulfide.* Microchimica Acta, 2015. **182**(9-10): p. 1803-1809.

[57] Y. Sun, K. He, Z. Zhang, A. Zhou, and H. Duan, *Real-time electrochemical detection of hydrogen peroxide secretion in live cells by Pt nanoparticles decorated graphene–carbon nanotube hybrid paper electrode.* Biosensors and Bioelectronics, 2015. **68**: p. 358-364.

[58] S. Campuzano and J. Wang, *Nanobioelectroanalysis based on carbon/inorganic hybrid nanoarchitectures.* Electroanalysis, 2011. **23**(6): p. 1289-1300.

[59] R.S. Dey, R.K. Bera, and C. Raj, *Nanomaterial-based functional scaffolds for amperometric sensing of bioanalytes.* Analytical and bioanalytical chemistry, 2013. **405**(11): p. 3431-3448.

[60] R. Warren, F. Sammoura, A. Kozinda, and L. Lin. *ALD ruthenium oxide-carbon nanotube electrodes for supercapacitor applications*. in *Micro Electro Mechanical Systems (MEMS), 2014 IEEE 27th International Conference on*. 2014. IEEE.

[61] I. Willner and B. Willner, *Biomolecule-based nanomaterials and nanostructures.* Nano letters, 2010. **10**(10): p. 3805-3815.

[62] G. Yang, B. Liang, Q. Zhu, Y. Hu, and X. Ye, *Comprehensive Study of the Effects of Nanopore Structures on Enzyme Activity for the Enzyme Based Electrochemical Biosensors Based on Molecular Simulation.* The Journal of Physical Chemistry A, 2016.

[63] F.R. Baptista, S. Belhout, S. Giordani, and S. Quinn, *Recent developments in carbon nanomaterial sensors.* Chemical Society Reviews, 2015. **44**(13): p. 4433-4453.

[64] M.M. Barsan, M.E. Ghica, and C.M. Brett, *Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: A review.* Analytica chimica acta, 2015. **881**: p. 1-23.

[65] L. Zhang, Z. Song, and K. Liew, *Optimal shape control of CNT reinforced functionally graded composite plates using piezoelectric patches.* Composites Part B: Engineering, 2016. **85**: p. 140-149.

[66] S. Abdalla, F. Al-Marzouki, A.A. Al-Ghamdi, and A. Abdel-Daiem, *Different technical applications of carbon nanotubes.* Nanoscale research letters, 2015. **10**(1): p. 358.

[67] K.E. Moore, D.D. Tune, and B.S. Flavel, *Double‐Walled Carbon Nanotube Processing.* Advanced Materials, 2015. **27**(20): p. 3105-3137.

[68] L. Kong and W. Chen, *Carbon Nanotube and Graphene‐based Bioinspired Electrochemical Actuators.* Advanced Materials, 2014. **26**(7): p. 1025-1043.

[69] A.-S. Michardière, C. Mateo-Mateo, A. Derré, M.A. Correa-Duarte, N. Mano, and P. Poulin, *Carbon Nanotube Microfiber Actuators with Reduced Stress Relaxation.* The Journal of Physical Chemistry C, 2016. **120**(12): p. 6851-6858.

[70] V. Palmre, J. Torop, M. Arulepp, T. Sugino, K. Asaka, A. Jänes, E. Lust, and A. Aabloo, *Impact of carbon nanotube additives on carbide-derived carbon-based electroactive polymer actuators.* Carbon, 2012. **50**(12): p. 4351-4358.

[71] X. Xie, L. Qu, C. Zhou, Y. Li, J. Zhu, H. Bai, G. Shi, and L. Dai, *An asymmetrically surface-modified graphene film electrochemical actuator.* ACS nano, 2010. **4**(10): p. 6050-6054.

[72] L. Basirico and G. Lanzara, *Moving towards high-power, high-frequency and low-resistance CNT supercapacitors by tuning the CNT length, axial deformation and contact resistance.* Nanotechnology, 2012. **23**(30): p. 305401.

[73] X. Sun, J. Jin, X. Wang, D. Cai, and M. Song, *Conductive behaviour and self-conductance characteristic of carbon nanotubes/functionalized graphene hybrid films.* Journal of nanoscience and nanotechnology, 2011. **11**(6): p. 5075-5082.

[74] V.R. Kumar, M.K. Majumder, A. Alam, N.R. Kukkam, and B.K. Kaushik, *Stability and delay analysis of multi-layered GNR and multi-walled CNT interconnects.* Journal of Computational Electronics, 2015. **14**(2): p. 611-618.

[75] K. Mustonen, P. Laiho, A. Kaskela, T. Susi, A.G. Nasibulin, and E.I. Kauppinen, *Uncovering the ultimate performance of single-walled carbon nanotube films as transparent conductors.* Applied Physics Letters, 2015. **107**(14): p. 143113.

[76] F. Stan, L. Sandu, and C. Fetecau. *Investigation on the Effect of Carbon Nanotubes Concentration on the Electrical and Rheological Properties of PP/MWCNTs Composites*. in *ASME 2015 International Manufacturing Science and Engineering Conference*. 2015. American Society of Mechanical Engineers.

[77] J. Garel, C. Zhao, R. Popovitz-Biro, D. Golberg, W. Wang, and E. Joselevich, *BCN nanotubes as highly sensitive torsional electromechanical transducers.* Nano letters, 2014. **14**(11): p. 6132-6137.

[78] S. Jiang, T. Shi, X. Zhan, S. Xi, H. Long, B. Gong, J. Li, S. Cheng, Y. Huang, and Z. Tang, *Scalable fabrication of carbon-based MEMS/NEMS and their applications: a review.* Journal of Micromechanics and Microengineering, 2015. **25**(11): p. 113001.

[79] X. Zang, Q. Zhou, J. Chang, Y. Liu, and L. Lin, *Graphene and carbon nanotube (CNT) in MEMS/NEMS applications.* Microelectronic Engineering, 2015. **132**: p. 192-206.

[80] X. Cao, Y. Cao, and C. Zhou, *Imperceptible and Ultraflexible P-Type Transistors and Macroelectronics Based on Carbon Nanotubes.* ACS nano, 2015. **10**(1): p. 199-206.

[81] K. Chen, W. Gao, S. Emaminejad, D. Kiriya, H. Ota, H.Y.Y. Nyein, K. Takei, and A. Javey, *Printed carbon nanotube electronics and sensor systems.* Advanced Materials, 2016. **28**(22): p. 4397-4414.

[82] E. Prati, M. De Michielis, M. Belli, S. Cocco, M. Fanciulli, D. Kotekar-Patil, M. Ruoff, D.P. Kern, D.A. Wharam, and J. Verduijn, *Few electron limit of n-type metal oxide semiconductor single electron transistors.* Nanotechnology, 2012. **23**(21): p. 215204.

[83] Y. Wang, T. Li, and H. Yang, *Nanofabrication, effects and sensors based on micro-electro-mechanical systems technology.* Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2013. **371**(2000): p. 20120315.

[84] M. Domonkos, T. Izak, L. Stolcova, J. Proska, and A. Kromka, *Fabrication of periodically ordered diamond nanostructures by microsphere lithography.* physica status solidi (b), 2014. **251**(12): p. 2587-2592.

[85] A. Kromka, T. Izak, M. Davydova, and B. Rezek. *Nanocrystalline diamond films for electronic monitoring of gas and organic molecules*. in *Advanced Semiconductor Devices & Microsystems (ASDAM), 2016 11th International Conference on*. 2016. IEEE.

[86] Y. Liu and K. Sun, *Protein functionalized nanodiamond arrays.* Nanoscale research letters, 2010. **5**(6): p. 1045.

[87] D. Cimen and T. Caykara, *Micro-patterned polymer brushes by a combination of photolithography and interface-mediated RAFT polymerization for DNA hybridization.* Polymer Chemistry, 2015. **6**(38): p. 6812-6818.

[88] A. Houlton, B.A. Connolly, A.R. Pike, and B.R. Horrocks, *DNA-Modified Single Crystal and Nanoporous Silicon.* DNA Nanotechnology: Methods and Protocols, 2011: p. 199-207.

[89] B.D. Choudhury, R. Casquel, M.J. Bañuls, F. Sanza, M. Laguna, M. Holgado, R. Puchades, A. Maquieira, C. Barrios, and S. Anand, *Silicon nanopillar arrays with SiO 2 overlayer for biosensing application.* Optical Materials Express, 2014. **4**(7): p. 1345-1354.

[90] L. Strambini, A. Longo, S. Scarano, T. Prescimone, I. Palchetti, M. Minunni, D. Giannessi, and G. Barillaro, *Self-powered microneedle-based biosensors for pain-free high-accuracy measurement of glycaemia in interstitial fluid.* Biosensors and Bioelectronics, 2015. **66**: p. 162-168.

[91] J.Y. Huang, L. Zhong, C.M. Wang, J.P. Sullivan, W. Xu, L.Q. Zhang, S.X. Mao, N.S. Hudak, X.H. Liu, and A. Subramanian, *In situ observation of the electrochemical lithiation of a single SnO_2 nanowire electrode.* Science, 2010. **330**(6010): p. 1515-1520.

[92] C. Lokhande, D. Dubal, and O.-S. Joo, *Metal oxide thin film based supercapacitors.* Current Applied Physics, 2011. **11**(3): p. 255-270.

[93] D. Samanta and A. Sarkar, *Immobilization of bio-macromolecules on self-assembled monolayers: methods and sensor applications.* Chemical Society Reviews, 2011. **40**(5): p. 2567-2592.

[94] J. Wang, *Electrochemical biosensing based on noble metal nanoparticles.* Microchimica Acta, 2012. **177**(3-4): p. 245-270.

[95] S.K. Arya and S. Bhansali, *Lung cancer and its early detection using biomarker-based biosensors.* Chemical reviews, 2011. **111**(11): p. 6783-6809.

[96] W. Suginta, P. Khunkaewla, and A. Schulte, *Electrochemical biosensor applications of polysaccharides chitin and chitosan.* Chemical reviews, 2013. **113**(7): p. 5458-5479.

[97] Y. Einaga, J.S. Foord, and G.M. Swain, *Diamond electrodes: diversity and maturity.* MRS Bulletin, 2014. **39**(06): p. 525-532.

[98] A. Zeng, V.F. Neto, J.J. Gracio, and Q.H. Fan, *Diamond-like carbon (DLC) films as electrochemical electrodes.* Diamond and Related Materials, 2014. **43**: p. 12-22.

[99] R.J. Nemanich, J.A. Carlisle, A. Hirata, and K. Haenen, *CVD diamond—Research, applications, and challenges.* MRS Bulletin, 2014. **39**(06): p. 490-494.

[100] S. Chandra, A.D. Miller, A. Bendavid, P.J. Martin, and D.K. Wong, *Minimizing fouling at hydrogenated conical-tip carbon electrodes during dopamine detection in vivo.* Analytical chemistry, 2014. **86**(5): p. 2443-2450.

[101] J. Roeser, N.F. Alting, H.P. Permentier, A.P. Bruins, and R. Bischoff, *Boron-doped diamond electrodes for the electrochemical oxidation and cleavage of peptides.* Analytical chemistry, 2013. **85**(14): p. 6626-6632.

[102] I. Shpilevaya and J.S. Foord, *Electrochemistry of methyl viologen and anthraquinonedisulfonate at diamond and diamond powder electrodes: The influence of surface chemistry.* Electroanalysis, 2014. **26**(10): p. 2088-2099.

[103] V. Petrakova, V. Benson, M. Buncek, A. Fiserova, M. Ledvina, J. Stursa, P. Cigler, and M. Nesladek, *Imaging of transfection and intracellular release of intact, non-labeled DNA using fluorescent nanodiamonds.* Nanoscale, 2016. **8**(23): p. 12002-12012.

[104] Z. Wang, Y. Yang, Z. Xu, Y. Wang, W. Zhang, and P. Shi, *Interrogation of Cellular Innate Immunity by Diamond-Nanoneedle-Assisted Intracellular Molecular Fishing.* Nano letters, 2015. **15**(10): p. 7058-7063.

[105] Y. Yu, L. Wu, and J. Zhi, *Diamond Nanowires: Fabrication, Structure, Properties and Applications*, in *Novel Aspects of Diamond*. 2015, Springer. p. 123-164.

[106] K. Bewilogua and D. Hofmann, *History of diamond-like carbon films—from first experiments to worldwide applications.* Surface and Coatings Technology, 2014. **242**: p. 214-225.

[107] H. Niakan, Q. Yang, and J. Szpunar, *Structure and properties of diamond-like carbon thin films synthesized by biased target ion beam deposition.* Surface and Coatings Technology, 2013. **223**: p. 11-16.

[108] M. Panda, R. Krishnan, T. Ravindran, A. Das, G. Mangamma, S. Dash, A. Tyagi, R. Chitra, S. Bhattacharya, and N. Sahoo. *Spectroscopic studies on diamond like carbon films synthesized by pulsed laser ablation*. in *AIP Conference Proceedings*. 2016. AIP Publishing.

[109] J. Vetter, *60years of DLC coatings: Historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications.* Surface and Coatings Technology, 2014. **257**: p. 213-240.

[110] C. Charitidis, *Nanomechanical and nanotribological properties of carbon-based thin films: a review.* International Journal of Refractory Metals and Hard Materials, 2010. **28**(1): p. 51-70.

[111] C. Chouquet, J. Gavillet, C. Ducros, and F. Sanchette, *Effect of DLC surface texturing on friction and wear during lubricated sliding.* Materials Chemistry and Physics, 2010. **123**(2): p. 367-371.

[112] L. Cui, Z. Lu, and L. Wang, *Toward low friction in high vacuum for hydrogenated diamondlike carbon by tailoring sliding interface.* ACS applied materials & interfaces, 2013. **5**(13): p. 5889-5893.

[113] Y. Tanaka, M. Furuta, K. Kuriyama, R. Kuwabara, Y. Katsuki, T. Kondo, A. Fujishima, and K. Honda, *Electrochemical properties of N-doped hydrogenated amorphous carbon films fabricated by plasma-enhanced chemical vapor deposition methods.* Electrochimica Acta, 2011. **56**(3): p. 1172-1181.

[114] M. Perny, J. Huran, V. Saly, M. Vary, J. Packa, and A. Kobzev, *Electrical and structural characterization of carbon based films prepared by RF-PECVD and ECR-PECVD techniques for photovoltaic applications.* Journal of Optoelectronics and Advanced Materials, 2014. **16**(3-4): p. 306-310.

[115] T.A. Silva, H. Zanin, P.W. May, E.J. Corat, and O. Fatibello-Filho, *Electrochemical performance of porous diamond-like carbon electrodes for sensing hormones, neurotransmitters, and endocrine disruptors.* ACS applied materials & interfaces, 2014. **6**(23): p. 21086-21092.

[116] S. Khatir, A. Hirose, and C. Xiao, *Characterization of physical and biomedical properties of nitrogenated diamond-like carbon films coated on polytetrafluoroethylene substrates.* Diamond and Related Materials, 2015. **58**: p. 205-213.

[117] Y. Mabuchi, T. Higuchi, and V. Weihnacht, *Effect of sp^2/sp^3 bonding ratio and nitrogen content on friction properties of hydrogen-free DLC coatings.* Tribology International, 2013. **62**: p. 130-140.

[118] M.A. Rahman, N. Soin, P. Maguire, R. D'Sa, S. Roy, C. Mahony, P. Lemoine, R. McCann, S. Mitra, and J. McLaughlin, *Structural and surface energy analysis of nitrogenated ta-C films.* Thin Solid Films, 2011. **520**(1): p. 294-301.

[119] S. Yamamoto, A. Kawana, H. Ichimura, and C. Masuda, *Relationship between tribological properties and sp^3/sp^2 structure of nitrogenated diamond-like carbon deposited by plasma CVD.* Surface and Coatings Technology, 2012. **210**: p. 1-9.

[120] A. Liu, E. Liu, G. Yang, W. Ma, and N. Khun. *Electrochemical behavior of gold nanoparticles modified nitrogen incorporated diamond-like carbon electrode and its application in glucose sensing*. in *Nanoelectronics Conference (INEC), 2010 3rd International*. 2010. IEEE.

[121] A. Liu, Q. Ren, T. Xu, M. Yuan, and W. Tang, *Morphology-controllable gold nanostructures on phosphorus doped diamond-like carbon surfaces and their electrocatalysis for glucose oxidation.* Sensors and Actuators B: Chemical, 2012. **162**(1): p. 135-142.

[122] R. Asakawa, S. Nagashima, Y. Nakamura, T. Hasebe, T. Suzuki, and A. Hotta, *Combining polymers with diamond-like carbon (DLC) for highly functionalized materials.* Surface and Coatings Technology, 2011. **206**(4): p. 676-685.

[123] E. Kaivosoja, S. Myllymaa, V.-P. Kouri, K. Myllymaa, R. Lappalainen, and Y.T. Konttinen, *Enhancement of silicon using micro-patterned surfaces of thin films.* European cells & materials, 2009. **19**: p. 147-157.

[124] K.-L. Ou, C.-C. Weng, E. Sugiatno, M. Ruslin, Y.-H. Lin, and H.-Y. Cheng, *Effect of nanostructured thin film on minimally invasive surgery devices applications: characterization, cell cytotoxicity evaluation and an animal study in rat.* Surgical endoscopy, 2016. **30**(7): p. 3035-3049.

[125] Y. Yin, K. Fisher, N.J. Nosworthy, D. Bax, R.J. Clarke, D.R. McKenzie, and M.M. Bilek, *Comparison on protein adsorption properties of diamond-like carbon and nitrogen-containing plasma polymer surfaces.* Thin Solid Films, 2012. **520**(7): p. 3021-3025.

[126] G. Leal, M.A. Fraga, G.W. Cardoso, A.S. da Silva Sobrinho, and M. Massi. *Effect of metal target power on the properties of co-sputtered Sn-DLC and W-DLC thin films*. in *Microelectronics Technology and Devices (SBMicro), 2015 30th Symposium on*. 2015. IEEE.

[127] M. Smietana, W.J. Bock, and J. Szmidt, *Evolution of optical properties with deposition time of silicon nitride and diamond-like carbon films deposited by radio-frequency plasma-enhanced chemical vapor deposition method.* Thin Solid Films, 2011. **519**(19): p. 6339-6343.

[128] Y. Tao, M. Endo, M. Inagaki, and K. Kaneko, *Recent progress in the synthesis and applications of nanoporous carbon films.* Journal of Materials Chemistry, 2011. **21**(2): p. 313-323.

[129] S. Sainio, T. Palomäki, N. Tujunen, V. Protopopova, J. Koehne, K. Kordas, J. Koskinen, M. Meyyappan, and T. Laurila, *Integrated carbon nanostructures for detection of neurotransmitters.* Molecular neurobiology, 2015. **52**(2): p. 859-866.

[130] V.T. Dang, D.D. Nguyen, T.T. Cao, P.H. Le, and N.M. Phan, *Recent trends in preparation and application of carbon nanotube–graphene hybrid thin films.* Advances in Natural Sciences: Nanoscience and Nanotechnology, 2016. **7**(3): p. 033002.

[131] S. Nardecchia, D. Carriazo, M.L. Ferrer, M.C. Gutiérrez, and F. del Monte, *Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: synthesis and applications.* Chemical Society Reviews, 2013. **42**(2): p. 794-830.

[132] V.D. Punetha, S. Rana, H.J. Yoo, A. Chaurasia, J.T. McLeskey, M.S. Ramasamy, N.G. Sahoo, and J.W. Cho, *Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene.* Progress in Polymer Science, 2016.

[133] E. Llobet, *Gas sensors using carbon nanomaterials: A review.* Sensors and Actuators B: Chemical, 2013. **179**: p. 32-45.

[134] W. Gu and G. Yushin, *Review of nanostructured carbon materials for electrochemical capacitor applications: advantages and limitations of activated carbon, carbide‐derived carbon, zeolite‐templated carbon, carbon aerogels, carbon nanotubes, onion‐like carbon, and graphene.* Wiley Interdisciplinary Reviews: Energy and Environment, 2014. **3**(5): p. 424-473.

[135] Y. He, W. Chen, C. Gao, J. Zhou, X. Li, and E. Xie, *An overview of carbon materials for flexible electrochemical capacitors.* Nanoscale, 2013. **5**(19): p. 8799-8820.

[136] Z. Wang and Z. Dai, *Carbon nanomaterial-based electrochemical biosensors: an overview.* Nanoscale, 2015. **7**(15): p. 6420-6431.

[137] M.E. Itkis, A. Pekker, X. Tian, E. Bekyarova, and R.C. Haddon, *Networks of Semiconducting SWNTs: Contribution of Midgap Electronic States to the Electrical Transport.* Accounts of chemical research, 2015. **48**(8): p. 2270-2279.

[138] C. Chen, Q. Xie, D. Yang, H. Xiao, Y. Fu, Y. Tan, and S. Yao, *Recent advances in electrochemical glucose biosensors: a review.* Rsc Advances, 2013. **3**(14): p. 4473-4491.

[139] H. Karimi-Maleh, F. Tahernejad-Javazmi, N. Atar, M.L.t. Yola, V.K. Gupta, and A.A. Ensafi, *A novel DNA biosensor based on a pencil graphite electrode modified with polypyrrole/functionalized multiwalled carbon nanotubes for determination of 6-mercaptopurine anticancer drug.* Industrial & Engineering Chemistry Research, 2015. **54**(14): p. 3634-3639.

[140] A. Walcarius, S.D. Minteer, J. Wang, Y. Lin, and A. Merkoçi, *Nanomaterials for bio-functionalized electrodes: recent trends.* Journal of Materials Chemistry B, 2013. **1**(38): p. 4878-4908.

[141] S. Pilehvar, J.A. Rather, F. Dardenne, J. Robbens, R. Blust, and K. De Wael, *Carbon nanotubes based electrochemical aptasensing platform for the detection of hydroxylated polychlorinated biphenyl in human blood serum.* Biosensors and Bioelectronics, 2014. **54**: p. 78-84.

[142] J.N. Tiwari, V. Vij, K.C. Kemp, and K.S. Kim, *Engineered carbon-nanomaterial-based electrochemical sensors for biomolecules.* ACS nano, 2015. **10**(1): p. 46-80.

[143] B.-R. Adhikari, M. Govindhan, and A. Chen, *Carbon nanomaterials based electrochemical sensors/biosensors for the sensitive detection of pharmaceutical and biological compounds.* Sensors, 2015. **15**(9): p. 22490-22508.

[144] E. Primo, F. Gutierrez, G. Luque, P. Dalmasso, A. Gasnier, Y. Jalit, M. Moreno, M. Bracamonte, M.E. Rubio, and M. Pedano, *Comparative study of the electrochemical behavior and analytical applications of (bio) sensing platforms based on the use of multi-walled carbon nanotubes dispersed in different polymers.* Analytica chimica acta, 2013. **805**: p. 19-35.

[145] J. Zhu, X.-Y. Wu, D. Shan, P.-X. Yuan, and X.-J. Zhang, *Sensitive electrochemical detection of NADH and ethanol at low potential based on pyrocatechol violet electrodeposited on single walled carbon nanotubes-modified pencil graphite electrode.* Talanta, 2014. **130**: p. 96-102.

[146] D. Kul, M.E. Ghica, R. Pauliukaite, and C.M. Brett, *A novel amperometric sensor for ascorbic acid based on poly (Nile blue A) and functionalised multi-walled carbon nanotube modified electrodes.* Talanta, 2013. **111**: p. 76-84.

[147] Y. Lin, K. Liu, C. Liu, L. Yin, Q. Kang, L. Li, and B. Li, *Electrochemical sensing of bisphenol A based on polyglutamic acid/amino-functionalised carbon nanotubes nanocomposite.* Electrochimica Acta, 2014. **133**: p. 492-500.

[148] B. Prieto-Simón, N. Bandaru, C. Saint, and N. Voelcker, *Tailored carbon nanotube immunosensors for the detection of microbial contamination.* Biosensors and Bioelectronics, 2015. **67**: p. 642-648.

[149] W. Sun, L. Cao, Y. Deng, S. Gong, F. Shi, G. Li, and Z. Sun, *Direct electrochemistry with enhanced electrocatalytic activity of hemoglobin in hybrid modified electrodes composed of graphene and multi-walled carbon nanotubes.* Analytica chimica acta, 2013. **781**: p. 41-47.

[150] Z. Taleat, A. Khoshroo, and M. Mazloum-Ardakani, *Screen-printed electrodes for biosensing: a review (2008–2013).* Microchimica Acta, 2014. **181**(9-10): p. 865-891.

[151] H. Huang, T. Chen, X. Liu, and H. Ma, *Ultrasensitive and simultaneous detection of heavy metal ions based on three-dimensional graphene-carbon nanotubes hybrid electrode materials.* Analytica chimica acta, 2014. **852**: p. 45-54.

[152] V. Mani, B. Devadas, and S.-M. Chen, *Direct electrochemistry of glucose oxidase at electrochemically reduced graphene oxide-multiwalled carbon nanotubes hybrid material modified electrode for glucose biosensor.* Biosensors and Bioelectronics, 2013. **41**: p. 309-315.

[153] M.R.R. Kahkha, M. Kaykhaii, M.S. Afarani, and Z. Sepehri, *Determination of mefenamic acid in urine and pharmaceutical samples by HPLC after pipette-tip solid phase microextraction using zinc sulfide modified carbon nanotubes.* Analytical Methods, 2016. **8**(30): p. 5978-5983.

[154] D. Xiao, P. Dramou, N. Xiong, H. He, H. Li, D. Yuan, and H. Dai, *Development of novel molecularly imprinted magnetic solid-phase extraction materials based on magnetic carbon nanotubes and their application for the determination of gatifloxacin in serum samples coupled with high performance liquid chromatography.* Journal of Chromatography A, 2013. **1274**: p. 44-53.

[155] A. Martín, M.Á. López, M.C. González, and A. Escarpa, *Multidimensional carbon allotropes as electrochemical detectors in capillary and microchip electrophoresis.* Electrophoresis, 2015. **36**(1): p. 179-194.

[156] E.P. Randviir and C.E. Banks, *Electrode substrate innovation for electrochemical detection in microchip electrophoresis.* Electrophoresis, 2015. **36**(16): p. 1845-1853.

[157] E. Garrido, C. Aymonier, L. Roiban, O. Ersen, C. Labrugère, P. Gaillard, and M. Lamirand-Majimel, *Noble metals supported on carbon nanotubes using supercritical fluids for the preparation of composite materials: A look at the interface.* The Journal of Supercritical Fluids, 2015. **101**: p. 110-116.

[158] C. Soldano, *Hybrid metal-based carbon nanotubes: Novel platform for multifunctional applications.* Progress in Materials Science, 2015. **69**: p. 183-212.

[159] C. Wang, T. Ding, Y. Sun, X. Zhou, Y. Liu, and Q. Yang, *Ni 12 P 5 nanoparticles decorated on carbon nanotubes with enhanced electrocatalytic and lithium storage properties.* Nanoscale, 2015. **7**(45): p. 19241-19249.

[160] L. Zhang, B. Wang, Y. Ding, G. Wen, S.B.A. Hamid, and D. Su, *Disintegrative activation of Pd nanoparticles on carbon nanotubes for catalytic phenol hydrogenation.* Catalysis Science & Technology, 2016. **6**(4): p. 1003-1006.

[161] S. Ata, T. Yamada, and K. Hata, *Relationship Between Primary Structure and Hansen Solubility Parameter of Carbon Nanotubes.* Journal of Nanoscience and Nanotechnology, 2017. **17**(5): p. 3310-3315.

[162] S.M. Fatemi and M. Foroutan, *Recent developments concerning the dispersion of carbon nanotubes in surfactant/polymer systems by MD simulation.* Journal of Nanostructure in Chemistry, 2016. **6**(1): p. 29-40.

[163] T. Fujigaya and N. Nakashima, *Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants.* Science and Technology of Advanced Materials, 2015. **16**(2): p. 024802.

[164] Q. Zhao, K. Yang, S. Zhang, B. Chefetz, J. Zhao, H. Mashayekhi, and B. Xing, *Dispersant selection for nanomaterials: Insight into dispersing functionalized carbon nanotubes by small polar aromatic organic molecules.* Carbon, 2015. **91**: p. 494-505.

[165] J. Ning, Y. Wang, Q. Wu, X. Zhang, X. Lin, and H. Zhao, *Novel supramolecular assemblies of repulsive DNA–anionic porphyrin complexes based on covalently modified multi-walled carbon nanotubes and cyclodextrins.* RSC Advances, 2015. **5**(27): p. 21153-21160.

[166] H. Van Nguyen, N.M. Tun, and E. Rakov, *Dispersion of carbon nanomaterials in an aqueous medium using a triton X-100 surfactant.* Russian Journal of Inorganic Chemistry, 2015. **60**(4): p. 536-540.

[167] B. Jo and D. Banerjee, *Enhanced specific heat capacity of molten salt-based carbon nanotubes nanomaterials.* Journal of Heat Transfer, 2015. **137**(9): p. 091013.

[168] Z. Karimi, P. Su, R. Oftadeh, H. Ebrahimi, R. Ghosh, and A. Vaziri, *Decontamination of surfaces exposed to single wall carbon nanohorns.* Journal of Environmental Chemical Engineering, 2016. **4**(3): p. 3409-3414.

[169] K. Komori, T. Terse-Thakoor, and A. Mulchandani, *Electrochemical properties of seamless three-dimensional carbon nanotubes-grown graphene modified with horseradish peroxidase.* Bioelectrochemistry, 2016. **111**: p. 57-61.

[170] E. Ramos, W.A. Pardo, M. Mir, and J. Samitier, *Dependence of carbon nanotubes dispersion kinetics on surfactants.* Nanotechnology, 2017. **28**(13): p. 135702.

[171] M. Shanbedi, S.Z. Heris, and A. Maskooki, *Experimental investigation of stability and thermophysical properties of carbon nanotubes suspension in the presence of different surfactants.* Journal of Thermal Analysis and Calorimetry, 2015. **120**(2): p. 1193-1201.

[172] N.S. Mani, S. Kim, K. Annam, D. Bane, and G. Subramanyam. *Creation of carbon nanotube based bioSensors through dielectrophoretic assembly*. in *SPIE Nanoscience+ Engineering*. 2015. International Society for Optics and Photonics.

[173] I. Sifuentes-Nieves, R. Rendón-Villalobos, A. Jiménez-Aparicio, B.H. Camacho-Díaz, G.F. Gutiérrez López, and J. Solorza-Feria, *Physical, physicochemical, mechanical, and structural characterization of films based on gelatin/glycerol and carbon nanotubes.* International Journal of Polymer Science, 2015. **2015**.

[174] A. TermehYousefi, S. Bagheri, S. Shahnazar, M.H. Rahman, and N.A. Kadri, *Computational local stiffness analysis of biological cell: High aspect ratio single wall carbon nanotube tip.* Materials Science and Engineering: C, 2016. **59**: p. 636-642.

[175] J. Xu, Y. Shingaya, Y. Zhao, and T. Nakayama, *In situ, controlled and reproducible attachment of carbon nanotubes onto conductive AFM tips.* Applied Surface Science, 2015. **335**: p. 11-16.

[176] L. Nienhaus, S. Wieghold, D. Nguyen, J.W. Lyding, G.E. Scott, and M. Gruebele, *Optoelectronic Switching of a Carbon Nanotube Chiral Junction Imaged with Nanometer Spatial Resolution.* ACS nano, 2015. **9**(11): p. 10563-10570.

[177] H. Yan, M. Cummings, F. Camino, W. Xu, M. Lu, X. Tong, N. Shirato, D. Rosenmann, V. Rose, and E. Nazaretski, *Fabrication and characterization of CNT-Based smart tips for synchrotron assisted STM.* Journal of Nanomaterials, 2015. **16**(1): p. 277.

[178] J. Choi, B.C. Park, S.J. Ahn, D.-H. Kim, J. Lyou, R.G. Dixson, N.G. Orji, J. Fu, and T.V. Vorburger, *Evaluation of carbon nanotube probes in critical dimension atomic force microscopes.* Journal of Micro/Nanolithography, MEMS, and MOEMS, 2016. **15**(3): p. 034005-034005.

[179] A.D. Slattery, C.J. Shearer, C.T. Gibson, J.G. Shapter, D.A. Lewis, and A.J. Stapleton, *Carbon nanotube modified probes for stable and high sensitivity conductive atomic force microscopy.* Nanotechnology, 2016. **27**(47): p. 475708.

[180] E. Palecek, *Oscillographic polarography of highly polymerized deoxyribonucleic acid.* Nature, 1960. **188**: p. 656-657.

[181] Z. Guo, X. Liu, Y. Liu, G. Wu, and X. Lu, *Constructing a novel 8-hydroxy-2'-deoxyguanosine electrochemical sensor and application in evaluating the oxidative damages of DNA and guanine.* Biosensors and Bioelectronics, 2016. **86**: p. 671-676.

[182] D. Ozkan-Ariksoysal, Y.U. Kayran, F.F. Yilmaz, A.A. Ciucu, I.G. David, V. David, M. Hosgor-Limoncu, and M. Ozsoz, *DNA-wrapped multi-walled carbon nanotube modified electrochemical biosensor for the detection of Escherichia coli from real samples.* Talanta, 2017.

[183] E.O. Fedorovskaya, E.K. Apartsin, D.S. Novopashina, A.G. Venyaminova, A.G. Kurenya, L.G. Bulusheva, and A.V. Okotrub, *RNA-modified carbon nanotube arrays recognizing RNA via electrochemical capacitance response.* Materials & Design, 2016. **100**: p. 67-72.

[184] W. Zhang, *Application of Fe3O4 nanoparticles functionalized carbon nanotubes for electrochemical sensing of DNA hybridization.* Journal of Applied Electrochemistry, 2016. **46**(5): p. 559-566.

[185] X. Liu, C. Du, D. Ni, Q. Ran, F. Liu, D. Jiang, and X. Pu, *A simple and sensitive electrochemical sensor for rapid detection of Clostridium tetani based on multi-walled carbon nanotubes.* Analytical Methods, 2016. **8**(47): p. 8280-8287.

[186] Y. Cai, F. Edin, Z. Jin, A. Alexsson, O. Gudjonsson, W. Liu, H. Rask-Andersen, M. Karlsson, and H. Li, *Strategy towards independent electrical stimulation from cochlear implants: Guided auditory neuron growth on topographically modified nanocrystalline diamond.* Acta Biomaterialia, 2016. **31**(0): p. 211-220.

[187] S. Dhall and N. Jaggi, *Hydrogen Gas Sensing Characteristics of Multiwalled Carbon Nanotubes Based Hybrid Composites.* Journal of Electronic Materials, 2016. **45**(1): p. 695-702.

[188] H.S. Kim, K.U. Jang, and T.W. Kim, *NO x gas detection characteristics in FET-type multi-walled carbon nanotube-based gas sensors for various electrode spacings.* Journal of the Korean Physical Society, 2016. **68**(6): p. 797-802.

[189] A. Cismaru, M. Aldrigo, A. Radoi, and M. Dragoman, *Carbon nanotube-based electromagnetic band gap resonator for CH4 gas detection.* Journal of Applied Physics, 2016. **119**(12): p. 124504.

[190] M. Asad, M.H. Sheikhi, M. Pourfath, and M. Moradi, *High sensitive and selective flexible H 2 S gas sensors based on Cu nanoparticle decorated SWCNTs.* Sensors and Actuators B: Chemical, 2015. **210**: p. 1-8.

[191] S. Liu, Z. Wang, Y. Zhang, C. Zhang, and T. Zhang, *High performance room temperature NO 2 sensors based on reduced graphene oxide-multiwalled carbon nanotubes-tin oxide nanoparticles hybrids.* Sensors and Actuators B: Chemical, 2015. **211**: p. 318-324.

[192] H. Zhang, J. Feng, T. Fei, S. Liu, and T. Zhang, *SnO 2 nanoparticles-reduced graphene oxide nanocomposites for NO 2 sensing at low operating temperature.* Sensors and Actuators B: Chemical, 2014. **190**: p. 472-478.

[193] S. Abdulla, T.L. Mathew, and B. Pullithadathil, *Highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection.* Sensors and Actuators B: Chemical, 2015. **221**: p. 1523-1534.

[194] S. Bai, C. Sun, H. Yan, X. Sun, H. Zhang, L. Luo, X. Lei, P. Wan, and X. Chen, *Healable, Transparent, Room‐Temperature Electronic Sensors Based on Carbon Nanotube Network‐Coated Polyelectrolyte Multilayers.* Small, 2015. **11**(43): p. 5807-5813.

[195] C. Piloto, F. Mirri, E.A. Bengio, M. Notarianni, B. Gupta, M. Shafiei, M. Pasquali, and N. Motta, *Room temperature gas sensing properties of ultrathin carbon nanotube films by surfactant-free dip coating.* Sensors and Actuators B: Chemical, 2016. **227**: p. 128-134.

[196] M.T. Humayun, R. Divan, Y. Liu, L. Gundel, P.A. Solomon, and I. Paprotny, *Novel chemoresistive CH4 sensor with 10 ppm sensitivity based on multiwalled carbon nanotubes functionalized with SnO2 nanocrystals.* Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2016. **34**(1): p. 01A131.

[197] J.M. Kauffmann and J.C. Viré, *Pharmaceutical and biomedical applications of electroanalysis.* Analytica Chimica Acta, 1993. **273**(1): p. 329-334.

[198] A.C. Ferrari and J. Robertson, *Interpretation of Raman spectra of disordered and amorphous carbon.* Phys. Rev. B, 2000. **61**(20): p. 14095-14107.

[199] Z.J. Ayres, S.J. Cobb, M.E. Newton, and J.V. Macpherson, *Quinone electrochemistry for the comparative assessment of sp2 surface content of boron doped diamond electrodes.* Electrochemistry Communications, 2016. **72**(0): p. 59-63.

[200] R. Wang, Y. Sun, Q. Yin, H. Xie, W. Li, C. Wang, J. Guo, Y. Hao, R. Tao, and Z. Jia, *The effects of metronidazole on Cytochrome P450 Activity and Expression in rats after acute exposure to high altitude of 4300 m.* Biomedicine & Pharmacotherapy, 2017. **85**(0): p. 296-302.

[201] H.B. Ammar, M.B. Brahim, R. Abdelhédi, and Y. Samet, *Boron doped diamond sensor for sensitive determination of metronidazole: Mechanistic and analytical study by cyclic voltammetry and square wave voltammetry.* Materials Science and Engineering: C, 2016. **59**(0): p. 604-610.

[202] D.M. Stanković and K. Kalcher, *Amperometric quantification of the pesticide ziram at boron doped diamond electrodes using flow injection analysis.* Sensors and Actuators B: Chemical, 2016. **233**(0): p. 144-147.

[203] T. Watanabe, S. Shibano, H. Maeda, A. Sugitani, M. Katayama, Y. Matsumoto, and Y. Einaga, *Fabrication of a Microfluidic Device with Boron-doped Diamond Electrodes for Electrochemical Analysis.* Electrochimica Acta, 2016. **197**(0): p. 159-166.

[204] T.A. Ivandini, T.N. Rao, A. Fujishima, and Y. Einaga, *Electrochemical Oxidation of Oxalic Acid at Highly Boron-Doped Diamond Electrodes.* Analytical Chemistry, 2006. **78**(10): p. 3467-3471.

[205] M. Brycht, K. Kaczmarska, B. Uslu, S.A. Ozkan, and S. Skrzypek, *Sensitive determination of anticancer drug imatinib in spiked human urine samples by differential pulse voltammetry on anodically pretreated boron-doped diamond electrode.* Diamond and Related Materials, 2016. **68**(0): p. 13-22.

[206] P.E. Jackson, D.P. Cooper, T.A. Meyer, M. Wood, A.C. Povey, and G.P. Margison, *Formation and persistence of O6-methylguanine in the mouse colon following treatment with 1,2-dimethylhydrazine as measured by an O6-alkylguanine-DNA alkyltransferase inactivation assay.* Toxicology Letters, 2000. **115**(3): p. 205-212.

[207] I. Sanjuán, A. Brotons, N. Hernández-Ibáñez, C.W. Foster, C.E. Banks, and J. Iniesta, *Boron-doped diamond electrodes explored for the electroanalytical detection of 7-methylguanine and applied for its sensing within urine samples.* Electrochimica Acta, 2016. **197**(0): p. 167-178.

[208] A. Brotons, L.A. Mas, J.P. Metters, C.E. Banks, and J. Iniesta, *Voltammetric behaviour of free DNA bases, methylcytosine and oligonucleotides at disposable screen printed graphite electrode platforms.* Analyst, 2013. **138**(18): p. 5239-5249.

[209] S. Chandra, A.D. Miller, A. Bendavid, P.J. Martin, and D.K.Y. Wong, *Minimizing Fouling at Hydrogenated Conical-Tip Carbon Electrodes during Dopamine Detection in Vivo.* Analytical Chemistry, 2014. **86**(5): p. 2443-2450.

[210] X. Ouyang, L. Luo, Y. Ding, B. Liu, D. Xu, and A. Huang, *Simultaneous determination of uric acid, dopamine and ascorbic acid based on poly(bromocresol green) modified glassy carbon electrode.* Journal of Electroanalytical Chemistry, 2015. **748**(0): p. 1-7.

[211] S.A. Skoog, P.R. Miller, R.D. Boehm, A.V. Sumant, R. Polsky, and R.J. Narayan, *Nitrogen-incorporated ultrananocrystalline diamond microneedle arrays for electrochemical biosensing.* Diamond and Related Materials, 2015. **54**(0): p. 39-46.

[212] J. Shalini, K.J. Sankaran, C.-L. Dong, C.-Y. Lee, N.-H. Tai, and I.N. Lin, *In situ detection of dopamine using nitrogen incorporated diamond nanowire electrode.* Nanoscale, 2013. **5**(3): p. 1159-1167.

[213] J. Shalini, Y.-C. Lin, T.-H. Chang, K.J. Sankaran, H.-C. Chen, I.N. Lin, C.-Y. Lee, and N.-H. Tai, *Ultra-nanocrystalline diamond nanowires with enhanced electrochemical properties.* Electrochimica Acta, 2013. **92**(0): p. 9-19.

[214] S. Chandra, A.D. Miller, and D.K.Y. Wong, *Evaluation of physically small p-phenylacetate-modified carbon electrodes against fouling during dopamine detection in vivo.* Electrochimica Acta, 2013. **101**: p. 225-231.

[215] Y. Qi, H. Long, L. Ma, Q. Wei, S. Li, Z. Yu, J. Hu, P. Liu, Y. Wang, and L. Meng, *Enhanced selectivity of boron doped diamond electrodes for the detection of dopamine*

and ascorbic acid by increasing the film thickness. Applied Surface Science, 2016. **390**: p. 882-889.

[216] W. Dai, M. Li, S. Gao, H. Li, C. Li, S. Xu, X. Wu, and B. Yang, *Fabrication of Nickel/nanodiamond/boron-doped diamond electrode for non-enzymatic glucose biosensor.* Electrochimica Acta, 2016. **187**: p. 413-421.

[217] J.K. McDonough and Y. Gogotsi, *Carbon Onions: Synthesis and Electrochemical Applications.* The Electrochemical Society Interface, 2013. **22**(3): p. 61-66.

[218] E. Peltola, N. Wester, K.B. Holt, L.-S. Johansson, J. Koskinen, V. Myllymäki, and T. Laurila, *Nanodiamonds on tetrahedral amorphous carbon significantly enhance dopamine detection and cell viability.* Biosensors and Bioelectronics, 2017. **88**: p. 273-282.

[219] H.-C. Wang and A.-R. Lee, *Recent developments in blood glucose sensors.* Journal of Food and Drug Analysis, 2015. **23**(2): p. 191-200.

[220] H. Du Toit and M. Di Lorenzo, *Electrodeposited highly porous gold microelectrodes for the direct electrocatalytic oxidation of aqueous glucose.* Sensors and Actuators B: Chemical, 2014. **192**: p. 725-729.

[221] S. Chandra, S. Siraj, and D.K. Wong, *Recent Advances in Biosensing for Neurotransmitters and Disease Biomarkers using Microelectrodes.* ChemElectroChem, 2017. **4**(4): p. 822-833.

[222] V. Scognamiglio, *Nanotechnology in glucose monitoring: advances and challenges in the last 10 years.* Biosensors and Bioelectronics, 2013. **47**: p. 12-25.

[223] K. ul Hasan, M.H. Asif, M.U. Hassan, M.O. Sandberg, O. Nur, M. Willander, S. Fagerholm, and P. Strålfors, *A miniature graphene-based biosensor for intracellular glucose measurements.* Electrochimica Acta, 2015. **174**: p. 574-580.

[224] M. Carbone, L. Gorton, and R. Antiochia, *An Overview of the Latest Graphene‐Based Sensors for Glucose Detection: the Effects of Graphene Defects.* Electroanalysis, 2015. **27**(1): p. 16-31.

[225] Z. Deng, H. Long, Q. Wei, Z. Yu, B. Zhou, Y. Wang, L. Zhang, S. Li, L. Ma, Y. Xie, and J. Min, *High-performance non-enzymatic glucose sensor based on nickel-microcrystalline graphite-boron doped diamond complex electrode.* Sensors and Actuators B: Chemical.

[226] H. Luo, G. Liu, R. Zhang, and S. Jin, *Phenol degradation in microbial fuel cells.* Chemical Engineering Journal, 2009. **147**(2–3): p. 259-264.

[227] M.A. Ajeel, M.K. Aroua, and W.M.A.W. Daud, *Preparation and characterization of carbon black diamond composite electrodes for anodic degradation of phenol.* Electrochimica Acta, 2015. **153**(0): p. 379-384.

[228] D.P. Dubal, S.H. Lee, J.G. Kim, W.B. Kim, and C.D. Lokhande, *Porous polypyrrole clusters prepared by electropolymerization for a high performance supercapacitor.* Journal of Materials Chemistry, 2012. **22**(7): p. 3044-3052.

[229] C. Hébert, E. Scorsone, M. Mermoux, and P. Bergonzo, *Porous diamond with high electrochemical performance.* Carbon, 2015. **90**: p. 102-109.

[230] L.W. Andersen, J. Mackenhauer, J.C. Roberts, K.M. Berg, M.N. Cocchi, and M.W. Donnino, *Etiology and therapeutic approach to elevated lactate.* Mayo Clinic proceedings, 2013. **88**(10): p. 1127-1140.

[231] S. Singh, A. Bhardawaj, R. Shukla, T. Jhadav, A. Sharma, and D. Basannar, *The handheld blood lactate analyser versus the blood gas based analyser for measurement of serum lactate and its prognostic significance in severe sepsis.* Medical Journal Armed Forces India, 2016. **72**(4): p. 325-331.

[232] M. Briones, E. Casero, M.D. Petit-Domínguez, M.A. Ruiz, A.M. Parra-Alfambra, F. Pariente, E. Lorenzo, and L. Vázquez, *Diamond nanoparticles based biosensors for efficient glucose and lactate determination.* Biosensors and Bioelectronics, 2015. **68**(0): p. 521-528.

[233] C. Yoshinaga-Itano, R.L. Baca, and A.L. Sedey, *Describing the trajectory of language development in the presence of severe to profound hearing loss: A closer look at children with cochlear implants versus hearing aids.* Otology & neurotology : official publication of the American Otological Society, American Neurotology Society [and] European Academy of Otology and Neurotology, 2010. **31**(8): p. 1268-1274.

[234] B.S. Wilson and M.F. Dorman, *Cochlear implants: a remarkable past and a brilliant future.* Hearing Research, 2008. **242**(0): p. 3-21.

[235] W. Zhang, K. Patel, A. Schexnider, S. Banu, and A.D. Radadia, *Nanostructuring of Biosensing Electrodes with Nanodiamonds for Antibody Immobilization.* ACS Nano, 2014. **8**(2): p. 1419-1428.

Figure legends

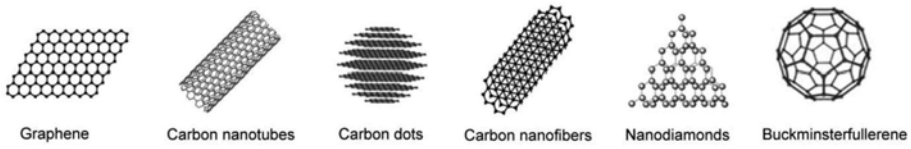


Figure 1 Schematic illustration of individual allotropes of CNTs. Reproduced from Ref. 136 with permission from the Royal Society of Chemistry.

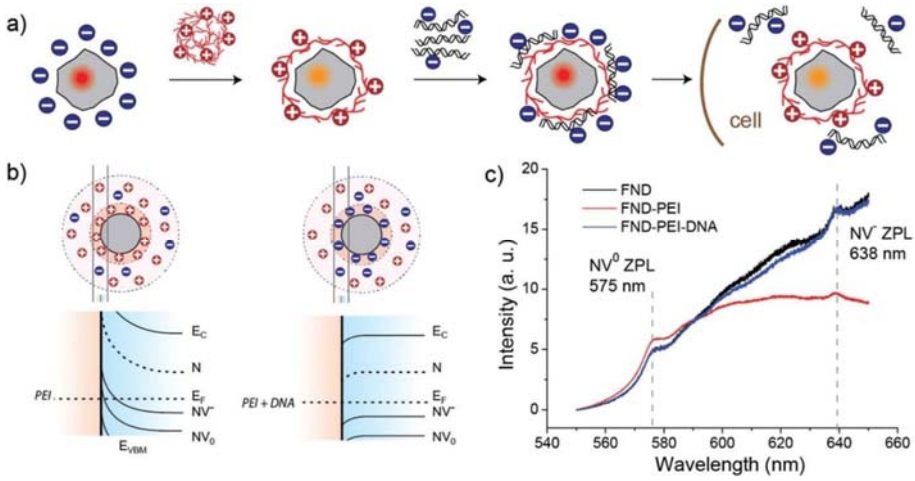


Figure 2 Example a fluorescent nano-diamond -based device. (a) Schematic of the formation of fluorescent nano-diamond – polyethylenimine –DNA complex based on electrostatic interactions and release of DNA after entering the cell. (b) Schematics of electrical charge density in the proximity of a fluorescent nano-diamond particle for fluorescent nano-diamond – polyethylenimine (left) and FND– polyethylenimine –DNA (right) complexes and the corresponding band bending of energetic levels in the diamond. (c) Photoluminescence spectra of oxidized fluorescent nano-diamond s and fluorescent nano-diamond – polyethylenimine and fluorescent nano-diamond – polyethylenimine –DNA complexes recorded in aqueous solution (FND concentration: 0.2 mg ml-1) using an excitation wavelength of 514 nm. Formation of fluorescent nano-diamond – polyethylenimine complex causes a significant decrease in nitrogen-vacancy – luminescence compared to oxidized fluorescent nano-diamond s. The level of nitrogen-vacancy – luminescence increases again upon binding of negatively charged DNA, which compensates for the positive charge of polyethylenimine. Reproduced from Ref. 103 with permission from Royal Society of Chemistry.

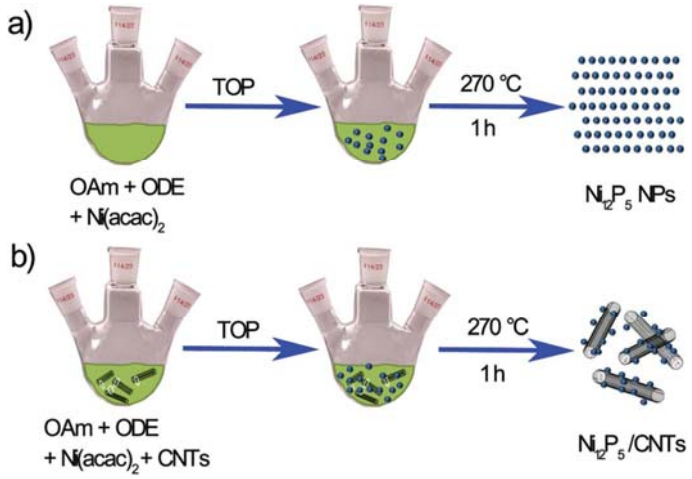


Figure 3 Illustration of the synthetic process for the monodisperse $Ni_{12}P_5$ nanoparticles (a) and the $Ni_{12}P_5$/CNT nanohybrids (b). Reproduced from Ref. 159 with permission from the Royal Society of Chemistry.

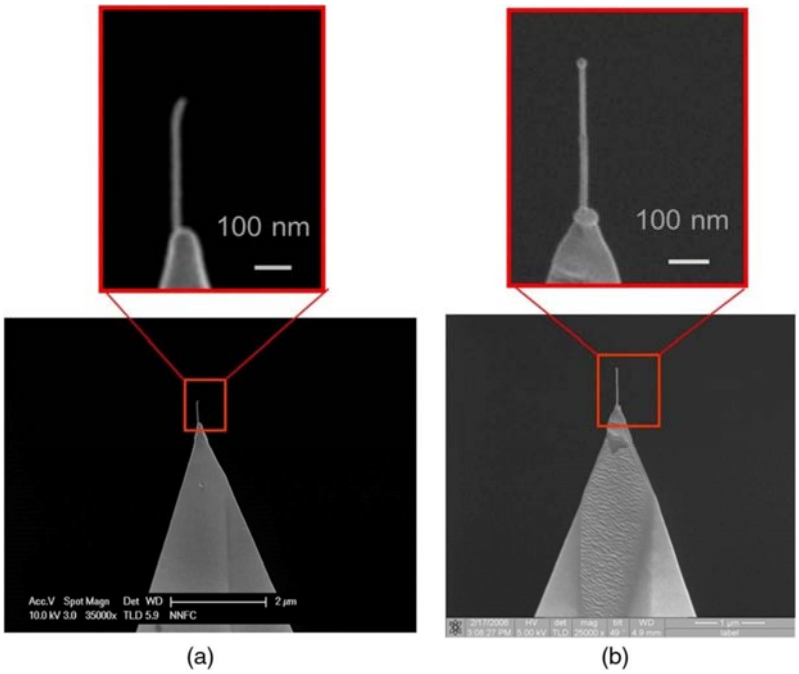


Figure 4 Scanning electron micrographs of fabricated nanoprobes for AFM: (a) J-tip and (b) B-tip types. These probes were fabricated to scan the sidewalls of a feature. Reproduced with permission from reference [179] Choi J, Park BC, Ahn SJ, Kim DH, Lyou J, Dixson RG, Orji NG, FU J, Vorburger TV, " Evaluation of carbon nanotube probes in critical dimension atomic force microscopes," Journal of Micro/Nanolithography, MEMS, and MOEMS, Mack CA, 15 (3) Number, 034005, (2016), Copyright Journal of

Micro/Nanolithography, MEMS, and MOEMS (2016) Society of Photo Optical Instrumentation Engineers.

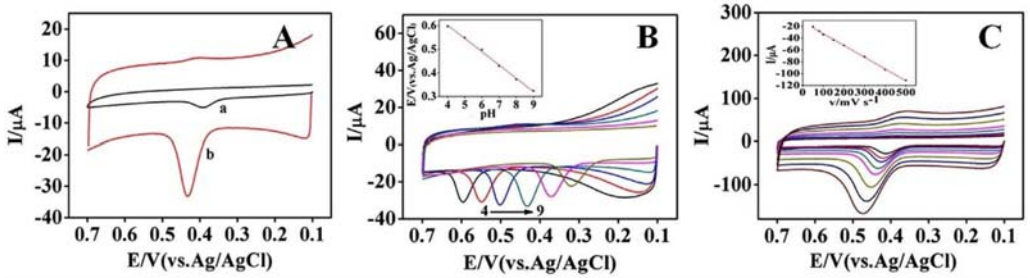


Figure 5 Shows (A) CV of bare GCE (a), MWCNTs/GCE (b) with 8.0 μM 8 –OhdG in 0.2 M PBS (pH 7.0), at 100 mVs-1. (B)CVs of 8 μM 8 OHdG on MWCNTs/GCE in 0.2M PBS at different pH:4,5,6,7,8,9; at 100mVs^{-1}. In set is the linear relationship of Epa vs. pH. (C) CVs of 8 μM 8 OHdGat MWCNTs/GCE with different scan rates (50 – 500mV^{-1}) in 0.2 M PBS (pH7.0). Inset is the linear relationship of Epa vs. ν. Reprinted from Biosensors and Bioelectronics, 86, Guo Z, Liu X, Wu G, Lu X, Constructing a novel 8-hydroxy-2′-deoxyguanosine electrochemical sensor and application in evaluating the oxidative damages of DNA and guanine, 671-676, Copyright (2016), with permission from Elsevier.

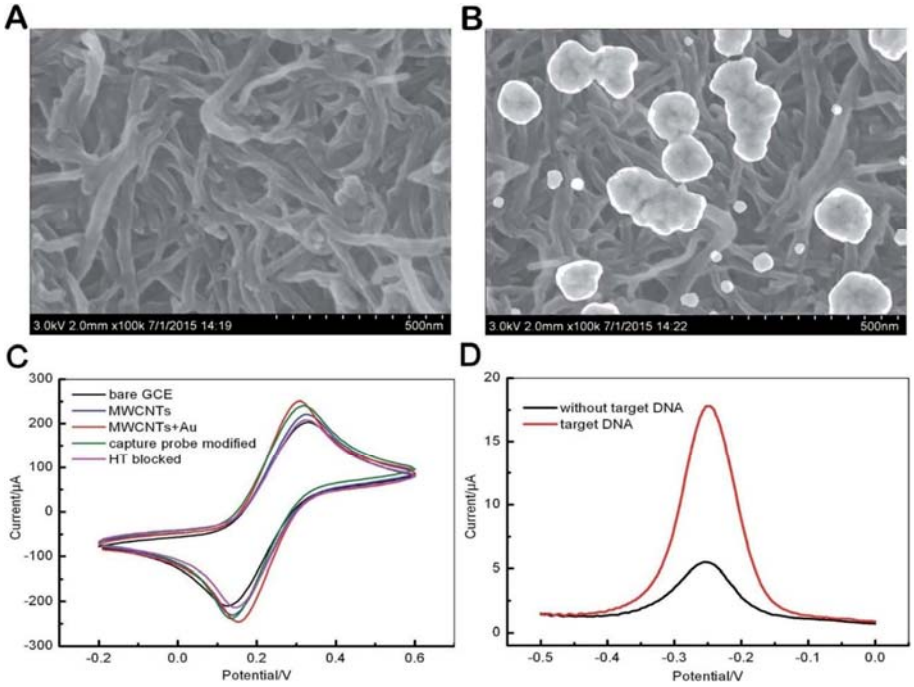


Figure 6 (A) SEM analysis of the morphology of MWCNTs; (B) SEM analysis of the morphology of MWCNTs/AuNPs; (C) CV measurements of the GCE after every processing

step; (D) pre-experiment of the sensor for the detection of target DNA (1.0 x 10^{-12} M). Reproduced from Ref. 185 with permission from the Royal Society of Chemistry.

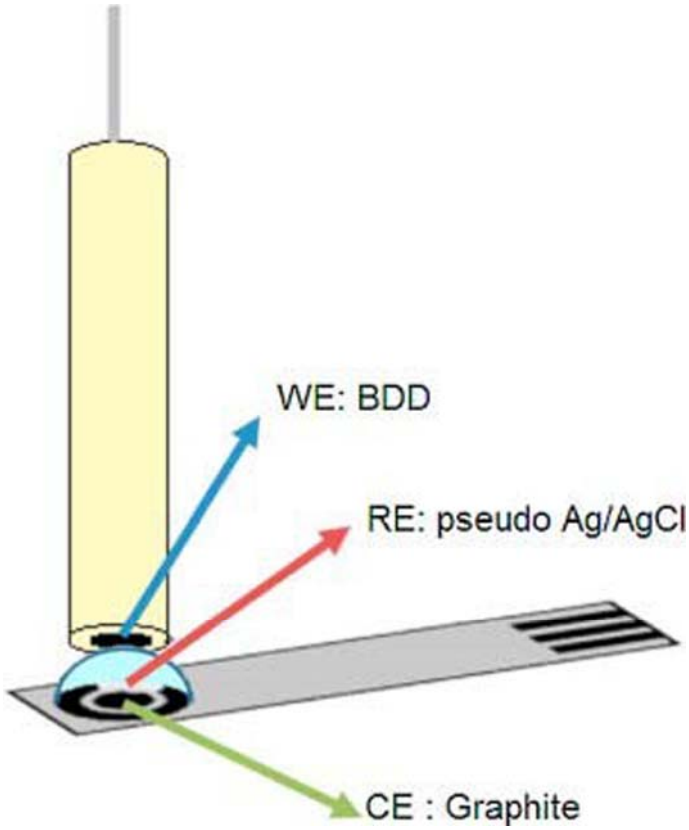


Figure 7 Electrochemical cell configuration used for the electroanalytical detection of 7-methylguanine [207] Reprinted from Electrochimica Acta, 138, Sanjuan I, Hernandez-Ibanez N, Foste CW, Banks Ce, Iniesta J, Boron-doped diamond electrodes explored for the electroanalytical detection of 7-methylguanine and applied for its sensing within urine samples, 671-676, Copyright (2016), with permission from Elsevier.

Author's corner

Dr Shaneel Chandra attained his PhD in Chemistry and Biomolecular Sciences from Macquarie University, Sydney in 2011 and is currently a lecturer/researcher at CQUniversity, Queensland. His research and HDR supervision focuses on biosensing of ultra-trace analytes in the physical environment and physiological systems. He has also previously been recognised for his research and teaching through the SPAS gold medal for Outstanding Thesis (MSc) in Science in 2002 and the Vice Chancellor's Excellence in Learning and Teaching Award in 2014 (USP).