
Review on carbon-derived, solid-state, micro and nano sensors for electrochemical sensing applications

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ARTICLE INFO

Article history:

Received 13 May 2009

Accepted 24 September 2009

Available online 8 October 2009

Keywords:

Carbon nanotube

Nanocrystalline diamond film

Diamond like carbon

Biosensor

Gas sensor

ABSTRACT

The aim of this review is to summarize the most relevant contributions in the development of electrochemical sensors based on carbon materials in the recent years. There have been increasing numbers of reports on the first application of carbon derived materials for the preparation of an electrochemical sensor. These include carbon nanotubes, diamond like carbon films and diamond film-based sensors demonstrating that the particular structure of these carbon material and their unique properties make them a very attractive material for the design of electrochemical biosensors and gas sensors.

Carbon nanotubes (CNT) have become one of the most extensively studied nanostructures because of their unique properties. CNT can enhance the electrochemical reactivity of important biomolecules and can promote the electron-transfer reactions of proteins (including those where the redox center is embedded deep within the glycoprotein shell). In addition to enhanced electrochemical reactivity, CNT-modified electrodes have been shown useful to be coated with biomolecules (e.g., nucleic acids) and to alleviate surface fouling effects (such as those involved in the NADH oxidation process). The remarkable sensitivity of CNT conductivity with the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors. These properties make CNT extremely attractive for a wide range of electrochemical sensors ranging from amperometric enzyme electrodes to DNA hybridization biosensors. Recently, a CNT sensor based fast diagnosis method using non-treated blood assay has been developed for specific detection of hepatitis B virus (HBV) (human liver diseases, such as chronic hepatitis, cirrhosis, and hepatocellular carcinoma caused by hepatitis B virus). The linear detection limits for HBV plasma is in the range $0.5\text{--}3.0\ \mu\text{L}^{-1}$ and for anti-HBVs $0.035\text{--}0.242\ \text{mg/mL}$ in a $0.1\ \text{M}\ \text{NH}_4\text{H}_2\text{PO}_4$ electrolyte solution. These detection limits enables early detection of HBV infection in suspected serum samples. Therefore, non-treated blood serum can be directly applied for real-time sensitive detection in medical diagnosis as well as in direct *in vivo* monitoring.

Synthetic diamond has been recognized as an extremely attractive material for both (bio-) chemical sensing and as an interface to biological systems. Synthetic diamond have outstanding electrochemical properties, superior chemical inertness and biocompatibility. Recent advances in the synthesis of highly conducting nanocrystalline-diamond thin films and nano wires have lead to an entirely new class of electrochemical biosensors and bio-inorganic interfaces. In addition, it also combines with development of new chemical approaches to covalently attach biomolecules on the diamond surface also contributed to the advancement of diamond-based biosensors. The feasibility of a capacitive field-effect EDIS (electrolyte-diamond-insulator-semiconductor) platform for multi-parameter sensing is demonstrated with an O-terminated nanocrystalline-diamond (NCD) film as transducer material for the detection of pH and penicillin concentration. This has also been extended for the label-free electrical monitoring of adsorption and binding of charged macromolecules. One more recent study demonstrated a novel bio-sensing platform, which is introduced by combination of a) geometrically controlled DNA bonding using vertically aligned diamond nano-wires and b) the superior electrochemical sensing properties of diamond as transducer material. Diamond nano-wires can be a new approach towards next generation electrochemical gene sensor platforms.

This review highlights the advantages of these carbon materials to promote different electron transfer reactions specially those related to biomolecules. Different strategies have been applied for constructing carbon material-based electrochemical sensors, their analytical performance and future prospects are discussed.

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1. Introduction

In some way, carbon materials touch every aspect of our daily lives. The emerging applications of carbon nanomaterials in electrochemical sensors have led to production of CNT, Crystalline Diamond (CD) and diamond like carbons (DLC) in a large scale. It will soon be possible to take advantage of demanding properties of novel carbon-derived materials to develop a myriad of new applications for chemical sensing. These carbon based materials can be used to operate at wider temperature and longer dynamic range with higher sensitivity even under harsh environmental operating conditions. A range of materials including platinum, gold, and various forms of carbon have thus been found useful for electrochemical detection [1–4]. CNT and diamond are two important polymorphs of carbon that have been widely employed as electrode materials for electrochemical sensing. This review paper mainly focuses on the use of carbon-derived materials, such as CNT and diamonds like NCD and DLC films for electrochemical sensing applications and their implications.

1.1. Carbon nanotubes (CNTs)

The discovery of C_{60} bucky-ball by Smalley's group [5] added a third kind of crystal structure for carbon besides the known forms including graphite and diamond. An analogous kind of crystal structure for carbon i.e., the CNT was found by Iijima [6] in due course of time. Since their discovery in 1991 [6], CNTs have attracted many scientists in the fields of physics, chemistry and materials sciences. CNTs are of tremendous current interest. The structure of CNTs is peculiar and different from graphite and traditional carbon fibers. CNTs are built from sp^2 carbon units, and are seamless structure with hexagonal honeycomb lattices. CNTs have closed topology and tubular structure that are typically several nanometers in diameter and many microns in length. There are two distinct structural families in CNTs, multi-wall carbon nanotubes (MWNTs) [6] and single-wall carbon nanotubes (SWNTs) [7]. MWNTs are composed of concentric and closed graphite tubules. Each tubule is made of a rolled graphite sheet that forms a range of diameters typically from 2 to 25 nm size with 0.34 nm distance between sheets close to the interlayer spacing in graphite. Whereas SWNT is made of a single graphite sheet rolled seamlessly, which is an individual cylinder of 1–2 nm diameter. SWNTs have the tendency to aggregate, usually forming bundles that consist of tens to hundreds of nanotubes in parallel and in contact with each other.

CNTs have unique mechanical and electronic properties combined with chemical stability [8]. They behave electrically as a metal or semiconductor depending on their structure based on their diameter

and helicity (symmetry of the two dimensional carbon lattice) [9]. SWNT is a well-defined system in terms of electronic properties and exhibit properties of quantum dots and wires at very low temperature by Coulomb blockade and single electron charging [10]. So far, wide ranges of potential and practical applications of CNTs have been reported, including chemical sensors [11–13], hydrogen energy storage [14], field emission materials [15], catalyst support [16], electronic devices [17], high sensitivity nanobalance for nanoscopic particles [18], and nanotweezers [19]. CNTs have some advantages over other bulky materials because of their small size with larger surface area, high sensitivity, fast response and reversible at room temperature that also serves as a gas sensor [20,21]. Additionally, CNT possess enhanced electron transfer property when used as electrodes in electrochemical reactions [22], and serves as a good solid support for easy protein immobilization that retains their native activity for use as potential biosensors [23].

The subtle electronic properties suggest that CNTs have the ability to mediate electron transfer reactions with electroactive species in solution when used as an electrode [22]. Therefore, CNT based electrodes have been used in electrochemical sensing [22–26]. Among the traditionally used electrode materials, CNTs showed better behavior than the others which also have good conducting ability and high chemical stability. CNT-based electrochemical transducers offer substantial improvements in the performance of amperometric enzyme electrodes, immunosensors and nucleic-acid sensing devices. The greatly enhanced electrochemical reactivity of hydrogen peroxide and NADH near the proximity or on the CNT-modified electrodes makes these nanomaterials extremely attractive for numerous oxidase- and dehydrogenase-based amperometric biosensors. Aligned CNT “forests” can act as molecular wires to allow efficient electron transfer between the underlying electrode and the redox centers of enzymes. The CNT transducer can greatly influence for enhancing the response of the biocatalytic reaction product and provide amplification platforms carrying multiple enzyme tags.

The CNTs have promising applications in the field of nanoelectromechanical systems (NEMS) that are devices integrating electrical and mechanical components with critical dimensions within 100 nm size [27,28]. CNTs have been considered as a potential alternate for silicon-based circuits due to their attractive electrical properties [27]. The interesting properties of CNTs are associated with their quasi-one-dimensional shape along with sp^2 and π -bonding between the carbon atoms. The π -electrons above and below the hexagonal graphene layer are free to move and form an electron band, producing the semi-metal electrical properties of graphite. However, for the nanotubes, the finite tube circumference restricts the number of allowed electron states. Hence, the semi-metal state of graphene is

altered and a band gap may open up at the Fermi energy. For larger diameter CNTs, the spacing between the lines is reduced and the maximum possible band gap decreases. The resistivity of a conducting material depends on the number of scatterers, number of carriers and the availability of states into which the electron or hole can be scattered. Hence, the perfect structure of the CNTs and the limited number of states are their advantageous abilities to transport ballistic electrical charge, i.e., electron transfer occurs without scattering over the distances of up to several micrometers depending on the quality of the tubes [28–30]. The downside is that it is more difficult to access these states due to their reduced number and specific configuration which leads to significant reflection at the contact–CNT interface. The number of transmitted electrons or holes depends on the number of states available. Each conducting state can transport one spin up and one spin down electron (or hole) giving a quantum conduction [30]. In this case, the voltage drops across the contacts but not along the tube. This applies to conduction through both metallic and semiconducting CNTs.

The ballistic transport and mechanical stability of the CNTs allow them to withstand high current densities up to 10^{10} A/cm², which is three to four orders of magnitude higher than most metals [31]. These unique properties have led to their use in areas as diverse as sensors [32], actuators [33], field-emitting flat panel displays [34], and energy and gas storage [35]. The fact that individual nanotubes can be either metallic conductors or semiconductors allowing them to be used to construct transistors and the connections between transistors, which make up the components of integrated circuits [28]. This can be a major boon as shrinking conventional complementary metal oxide semiconductor (CMOS) silicon transistors is approaching fundamental physical limits [27]. The potential implementation of these CNT-based circuits will allow for the continued reduction in transistor dimensions which is an important factor for increasing integrated circuit (IC) performance. Not only are the electrical properties of interest, CNTs also exhibit remarkable mechanical properties possessing a tensile strength greater than any other known materials. The properties of CNTs are strongly dependent on the chirality and the tube diameter [29]. For single-walled CNTs, about one third of the possible tube conformations are metallic, whereas, the remaining two thirds are semiconducting. The band gap of semiconducting SWNTs is inversely proportional to the diameter and corresponds to 0.8 eV for a tube with a diameter of 1 nm. SWNTs with diameters up to 5 nm and as small as 0.4 nm have been observed, but the diameter is typically between 0.7 nm and 2 nm providing band gaps in a range that is interesting for transistor and diode applications. MWNTs with diameters up to 100 nm have been observed although their diameters are usually around 10–20 nm [27].

1.2. Diamond

Diamond has attracted significant attention because diamond is the best known electrochemical transducer owing to its chemical stability, low background current, wide potential window, and outstanding bio-compatibility [36,37]. Applied materials such as Si, [38] SiO₂, [39] gold, [40] glassy carbon, [41] SnO₂ [42] and ZnO₂, [43] do not possess desired chemical stability and reproducibility of bio-chemical surfaces in electrolyte solutions. Only diamond is known to be outstanding with respect to electrochemical properties [37,44,45]. Its electrochemical background current in phosphate buffer is ten times lower than Au and about 100 times lower than glassy carbon. Diamond has a wide working window due to large over-potentials for hydrogen and oxygen evolution. A typical window of 3.25 V or greater is normal for high-quality films. Diamond can be n- and p-type doped from insulating to semiconducting to metallic, thereby changing from transparent (optical gap of 5.47 eV) to black. The surface of diamond shows unique properties as it can be terminated with hydrogen, with oxygen and OH group which allows optimizing the electronic

properties of the solid/electrolyte interface [46–48]. Diamond surfaces are hydrophobic in case of H termination and hydrophilic for O-termination. In addition, diamond is known to be chemically inert, [44] bio-compatible [49–51] and shows strongest bonding stability to DNA [39]. Besides its unprecedented utilization in tool industry and biology, many attempts are now being undertaken to put diamond in life science, sensor technology or electronics into practice. Progress in the broad application of diamond in life science devices was delayed because of high costs for production or refinement. Development of novel technologies not only expedited the synthesis of NCD, which exhibits similar remarkable properties as single crystal diamond at a reasonable price, yet more than that it has opened new avenues for future diamond research. The latter clearly calls for innovative product development to be commercialized in a broad area of applications in the near future.

1.3. Diamond-like carbon (DLC)

Carbon is well-known to crystallize in the forms of diamond (sp³) or graphite (sp²). Most of the carbon surfaces are chemically very stable and hence they are inert species under static conditions. These can interact with liquids or gases under the influence of sliding contacts such as terminating bonds on the surface. DLC is a non-crystalline carbon known as an amorphous carbon with a high fraction of diamond-like (sp³) bonds, and it is also named to be an amorphous hydrogenated carbon (a-C:H). Typically, thin films of hydrogen-free DLCs with a very high sp³ configuration can be prepared by filtered cathodic vacuum arc, pulsed laser deposition, or mass selected ion beam deposition [52]. On the other hand, hydrogenated amorphous carbon with sp² configuration is usually made by plasma enhanced chemical vapour deposition (PECVD) [53–56] or reactive sputtering [57,58]. The sp³ bonding is generated by ensuring that the deposition flux contains a sizeable fraction of medium energy ions with an energy approximately of 100 eV [59]. DLC has some unique properties, such as high elastic modulus, high mechanical hardness, very low surface roughness, and chemical inertness that makes it a valuable material for applications. It is also a semiconductor with a band gap, which can be varied from approximately 1 to 4 eV [60].

Diamond-like-carbon films constitute a new research area in electrochemistry. They have been used as electrodes in electrochemical microgravimetry on quartz crystal electrodes [60] as nitrogenated DLC films (N:DLC) for metal tracing analysis [61] and as coatings for polycarbonate membranes used as selective barriers in glucose oxidase biosensors [62,63].

Amorphous DLC electrodes has been reported as a glucose amperometric biosensor [56,64] and DLC microelectrodes for medical diagnosis of human immunodeficiency virus (HIV), human hepatitis B virus (HBV), and human hepatitis C virus (HCV) [65]. Depending on the deposition process and conditions, the Carbon-sp³/Carbon-sp² hybridization ratio may be adjusted and controlled and can be doped to form conductive material thus allowing tailoring the film properties depending on the application. Due to these properties, it has found applications in variety of areas such as electronic, optical, mechanical and biomedical applications [64].

2. CNT for chemical sensing

2.1. Electrochemical sensors based on CNT

Nanotechnology provides the ability to work at the nano level, atom by atom, to create large structure with fundamentally new molecular organization. CNTs belong to one class of nanostructured materials that has received much attention due to their remarkable mechanical and unique electronic properties as well as chemical stability and excellent heat conduction. CNTs have a large surface-to-

volume ratio with the diameter of a few nanometers and length up to 100 μm so that they form an extremely thin wire, which is a unique one in the carbon family with the hardness of diamond and the conductivity of graphite. Diamond is the hardest substance found in nature and is an insulator, but graphite is one of the softest conducting materials (pencils use graphite, and graphite is also often used as a lubricant to allow two surfaces to slide freely). Because the electronic property of CNTs is a strong function of their atomic structure and mechanical deformations, such relationships make them useful when developing extremely small sensors that are sensitive to the chemical and mechanical or physical environment.

Electrochemistry implies the transfer of charge from one electrode to another electrode. This means that at least two electrodes constitute an electrochemical cell to form a closed electrical circuit. Another important general aspect of electrochemical sensors is that the charge transport within the transducer part of the whole circuit is always electronic. On the other hand, the charge transport in the sample can be electronic, ionic, or mixed. Due to the curvature of carbon graphene sheet in nanotubes, the electron clouds change from a uniform distribution around the C–C backbone in graphite to an asymmetric distribution inside and outside the cylindrical sheet of the nanotube. When the electron clouds are distorted, a rich π -electron conjugation forms outside the tube, therefore making the CNT electrochemically active [66]. Electron donating and withdrawing molecules such as NO_2 , NH_3 , and O_2 will either transfer electrons to or withdraw electrons from SWNTs. Thereby giving SWNTs more charge carriers or holes, which increase or decrease the SWNT conductance [66].

Recent studies demonstrated that CNT can enhance the electrochemical reactivity of important biomolecules [67–70], and can promote the electron-transfer reactions of proteins (including those where the redox center is embedded deep within the glycoprotein shell) [71,72]. In addition to enhanced electrochemical reactivity, CNT-modified electrodes have been shown useful to accumulate important biomolecules (e.g., nucleic acids) [73] and to alleviate surface fouling effects (such as those involved in the NADH oxidation process) [68]. The remarkable sensitivity of CNT conductivity to the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors. These properties make CNT extremely attractive for a wide range of electrochemical biosensors ranging from amperometric enzyme electrodes to DNA hybridization biosensors. To take advantages of the remarkable properties of these unique nanomaterials in such electrochemical sensing applications, the CNT need to be properly functionalized and immobilized. There are different ways for confining CNT onto electrochemical transducers. Most commonly, this is accomplished using CNT-coated electrodes [74–77] or using CNT/binder composite electrodes [78–80]. The CNTs-driven electrocatalytic effects and the increasing use of modified CNTs for electroanalytical applications have been recently reviewed [77]. Moreover, electrochemical detection using CNTs-modified electrodes as detecting devices in separation techniques such as high performance liquid chromatography (HPLC) or capillary electrophoresis (CE) have also been documented [77]. CNTs play a significant role in sensing performances of electrochemical biosensors including enzyme electrodes, DNA biosensors and immunosensors [77]. Progress toward functionalization of SWNTs with metal nanoparticles using electrochemical methods and the applications of metal decorated CNTs in energy related applications have also been recently reviewed [81]. Here, the use of electrodeposition to modify SWNTs in order to facilitate applications in areas related to catalysis and sensing has been highlighted [81].

2.1.1.1. CNT-based amperometric transducers

The low solubility of SWNTs is another major challenge to mass production of SWNT-based devices. This insolubility is due in large part to strong Vander Waals interactions between nanotubes, which

results in aggregation. Therefore, after purification, the solubility of SWNT material is improved by use of various surfactants. This method preserves the structure and properties of SWNTs to a much greater extent than covalent modification. Surfactants that show promise in this process include DNA [82,83], polymers [84], and various detergents [85]. Sodium dodecyl sulfate (SDS) is one of the most common surfactants used to form aqueous suspensions of SWNTs. SDS coats SWNTs with micelles, forming a hydrophobic core and hydrophilic surface, thus assisting in homogenization in water. After the addition of the surfactant, sonication (bath or cup-horn) is used to disperse SWNTs in the solution. The micelles can then be removed in subsequent rinsing steps. In another approach, the ability of Nafion to solubilize CNT provides a useful avenue for preparing CNT-based electrode transducers for a wide range of sensing application [74]. The electroactivity of hydrogen peroxide (with detection limit down to 25 nM) can be obtained by dispersing platinum nanoparticles in the Nafion/CNT coating [86].

Simple modified electrode designs can be obtained by incorporation of a small volume of CNTs dispersion onto a glassy carbon electrode [87–89]. Methods for the preparation of homogeneous dispersions of CNTs suitable for processing into thin films can be found in some recent reports [90,91]. A comparison of different SWNTs dispersing strategies has been demonstrated, which involves the use of organic solvents and charged polymers (Nafion and Chitosan). This has been applied for preparation of modified GC (glassy carbon) electrodes toward hydrogen peroxide detection and showed that the best performance was obtained with a film cast from a chitosan solution [91].

An effective CNT coating can be obtained by aligning short SWNT to an electrode by self-assembly. The vertically aligned SWNT act as molecular wires to allow electrical communication between the underlying electrode and a redox enzyme [71,72]. The electrochemical determination of glutathione at well-aligned CNT arrays showed excellent electrochemical activity and good anti-fouling property for direct oxidation of glutathione [92].

Another important application of carbon nanotubes is their use as nanoprobe. Carbon nanoprobe are used as tips of atomic force microscope (AFM) or scanning tunneling microscope (STM) [93]. The CNT tips offer several advantages [94]: i) they have intrinsically small diameters ii) high ratio aspects that allow them to probe deep crevices and trench structures [93] iii) they can buckle elastically that limits the force applied by the AFM probe and reduce deformation and damage to biological and organic samples [95] and iv) they can be modified at their ends to create functional probes (as shown in Fig. 1) [96]. The use of functionalized nanotubes as AFM tips has opened up the applications of molecular recognition and chemically sensitive imaging in chemistry and biology. An AFM tip of CNT has been used for imaging of nanostructures [97], biological molecules such as DNA, and amyloid- β -protofibrils (relate to Alzheimer's disease) [98]. CNT tips can get higher resolution than general Si or metal tips. Lin and coworkers developed amperometric biosensors based on CNT-nanoelectrode ensembles [99]. Koehne et al. fabricated low-density CNT arrays on silicon chips using a bottom-up approach [100]. The lithographic patterning, metallization of the electrical contacts, deposition of a catalyst and CNT growth were made by PECVD. Electrochemical detection for microchip carbon electrode has shown to be very adequate due to its high sensitivity, low cost and miniaturization capability [101]. The application of CNTs-based detectors for microchip carbon electrode was introduced in a seminal work by Wang et al., and it has been reviewed by performing a comparison of the use of SWNTs, MWNTs and graphite powder films on GC, Au, and Pt electrode surfaces [102,103].

2.1.1.2. CNT-based electrochemical DNA sensors

The combination of CNT with DNA has attracted the attention of several research groups recently. DNA chains have been used to create

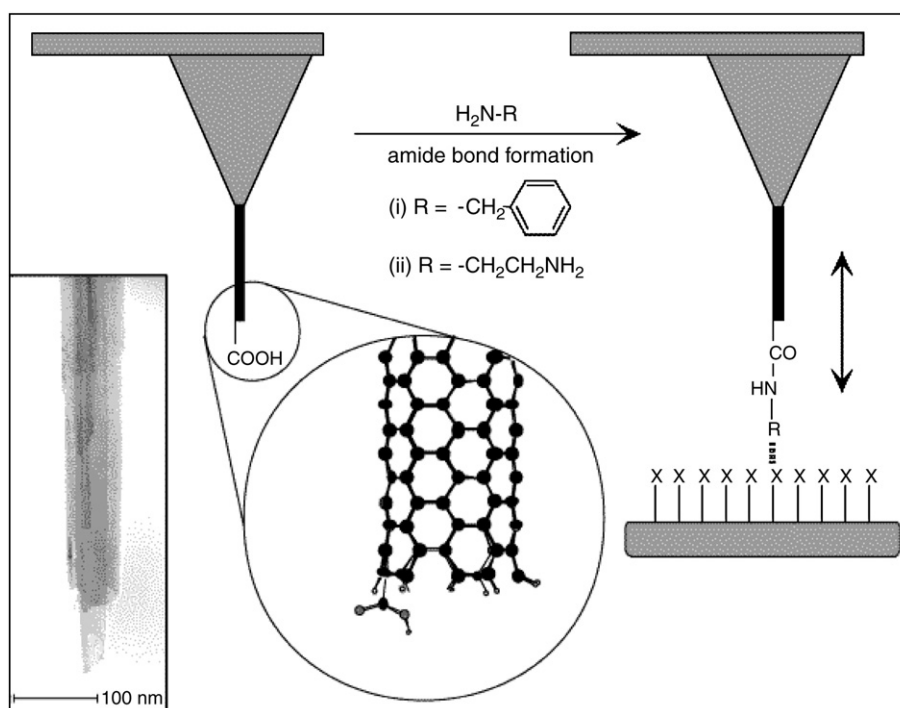


Fig. 1. Representation of functionalized carbon nanotube tips. The diagram illustrates the modification of a nanotube tip by coupling an amine (RNH_2) to a pendant carboxyl group [96].

various functional structures and devices through the sequence-specific pairing interactions. The DNA-based biomolecular recognition principle has been applied to CNTs to construct nanotube electronic devices as well as CNT–DNA electrochemical sensors. DNA biosensors based on nucleic acid recognition processes are rapidly being developed towards the goal of rapid, simple, and inexpensive testing of genetic and infectious diseases. Electrochemical hybridization biosensors rely on the immobilization of a single-stranded (ss-)DNA probe onto the transducer surface that converts the duplex formation into a useful electrical signal [104]. The performance of such devices can greatly benefit from the use of CNT. Such improvements are attributed to enhanced detection of the target guanine or of the product of an enzyme label, as well as to the use of CNT carrier platforms. The bifunctional chemical structure of CNTs would facilitate the selective attachment of multiple DNA sequences using two distinct DNA–CNT linking strategies. In one strategy, the free carboxyl groups of CNTs are attached with amine terminated single stranded DNA oligonucleotides in a CNT array using amide coupling chemistry in aqueous/organic solvent mixtures. The second strategy involves the attachment of oligonucleotides to the sidewalls of the CNTs through hydrophobic interactions.

Guo et al. [105] described the electrochemical characteristics of the immobilization of both double-stranded and single stranded calf thymus DNA molecules on the surface of MWNTs. The individual CNTs can be functionalized with special selectivity and can be used to differentiate between the two DNA sequences. The concept of using DNA to direct the assembly of nanotubes into nanoscale devices has attracted attention, because of its potential to assemble a multicomponent system in one step by using different base sequence for each component. The reactive sites on the CNTs were created by the acid treatment to introduce the carboxyl groups on their tips. DNA molecules with functional linkers are then coupled to the carboxyl groups on the CNTs.

Chen et al. developed a multistep method to covalently functionalize MWNTs with DNA oligonucleotides [106]. Thus, the bioconjugates of carbon nanomaterials and DNA will have potential uses in many areas due to the combination of unusual structure of carbon

nanomaterials and bioactivity of DNA [107]. Hazani et al. reported the confocal fluorescence imaging of SWNT–DNA adducts obtained by carbodiimide assisted coupling of amine functionalized oligonucleotides to oxidized SWNTs [108]. CNTs have been recently used as transducers for enhanced electrical detection of DNA hybridization [109]. The DNA sensing application requires high sensitivity through amplified transduction of the oligonucleotide interaction. The wrapping of CNTs in DNA results in some interesting effects. The DNA nanotube species are highly soluble in water removing the requirement for surfactants. Also the negative charges on the phosphate group of DNA results in the charging of DNA nanotube species. The unique property of the specific molecular recognition of DNA coupling with SWNTs and hybridizing these macromolecular wires will provide a versatile means of incorporating SWNTs into larger electronic devices. This can be accomplished by recognition-based assembly and using SWNTs as probes in biological systems by sequence-specific attachment [110].

The most ideal approach for DNA immobilization in CNTs is covalent binding on a solid surface via a single point attachment. Most of the applications of immobilized oligonucleotide are based on the hybridization between immobilized oligonucleotide and its complementary DNA sequence [111]. Cai et al. reported the application of CNTs to the fabrication of an electrochemical DNA biosensor for the specific DNA sequence detection [112]. Fig. 2 shows the schematic representation of the enhanced electrochemical detection of DNA hybridization based on the MWNTs–COOH constructed biosensor [112]. Lu et al. discussed in detail about the system used as an electronic switch or as a sensor device for ultra fast DNA sequencing [113].

The controlled self-assembly of CNTs was recently achieved by interphasing the CNTs with biomolecules. This approach has considerable potential for driving self-assembly of CNT-based devices in the light of the immense richness of biological recognition. The approach involves two steps. In the first step, a self-assembled nanolayer of single stranded DNA is adsorbed onto Au contacts by reaction with thiol terminated oligonucleotides, and in the next step, the oxidized CNTs modified with oligonucleotides of the complementary sequence

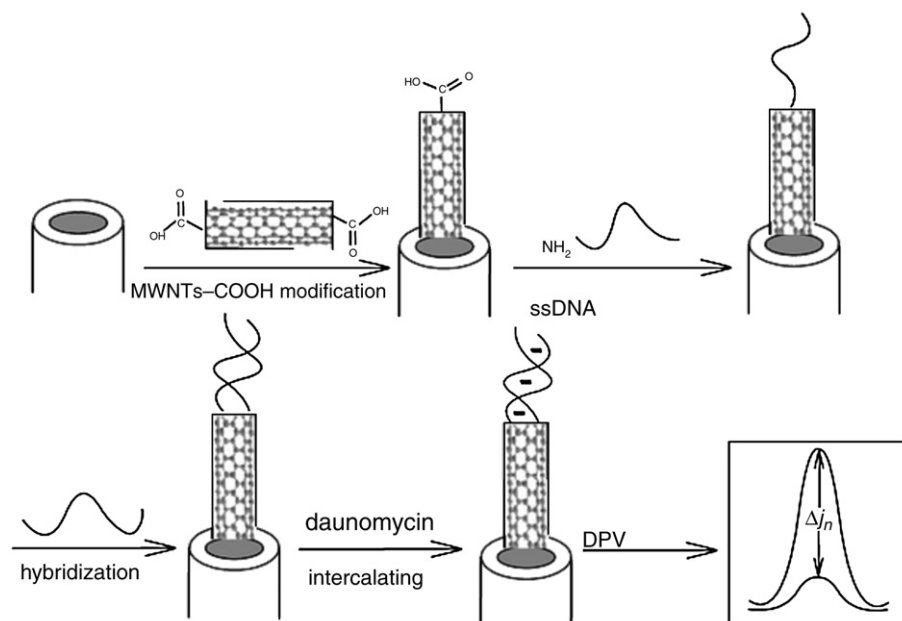


Fig. 2. Schematic representation of enhanced electrochemical detection of DNA hybridization based on the MWNTs-COOH constructed DNA biosensor [112].

are allowed to hybridize with the DNA located on the Au contacts. Wang et al. reported a novel DNA immobilization strategy, in which the DNA probes are adsorbed on self-assembled MWNTs [114]. They assayed the hybridization by the changes in the voltammetric peak of the indicator methylene blue and the results showed that the DNA biosensors based on the self-assembled MWNTs have a higher hybridization efficiency than that based on random MWNTs. Li et al. demonstrated that a wide range of multicomponent structures of CNTs can be constructed by DNA directed self-assembly of CNTs and gold nanoparticles [115]. Banerjee and Wong reported that by varying the nature of the organic capping groups on the nanocrystal surface and the organic bifunctional linkers, it is possible to modulate interactions between the nanotubes and the nanocrystals with implications for self-assembly [116]. Wang et al. developed DNA biosensors based on the self-assembly of carbon nanotubes [114]. The functionalization/grafting of DNA onto SWNTs and MWNTs with or without self-assembly which can be employed in fabricating biosensors for selective recognition of DNA recently reviewed by Daniel et al. [117].

Glassy carbon electrodes (GCE) modified with CNTs has been shown useful to facilitate the adsorptive accumulation of the guanine nucleobase and greatly enhances its oxidation signal [73]. The dramatic amplification of the guanine signal has been combined with a label-free electrical detection of DNA hybridization [118–122]. An enhancement of the guanine DNA response was shown using MWNT paste electrodes [118] and SWNT-coated GCE [123]. The MWNTs-modified GCE has been used for determination of DNA and DNA bases [124–127]. MWNTs-modified carbon paste electrode has been used for the electrocatalytic oxidation of bergenin, a herbal medicine, for the determination of its concentration in medicinal tablets [128]. The MWNTs-modified GCE have also been employed for the determination of anti-thalassemia and anti-HIV replication drugs, deferiprone through electrocatalytic oxidation has also been reported [129]. An array of vertically aligned MWNT embedded in SiO₂ has been shown to be useful for ultrasensitive detection of DNA hybridization [130]. DNA hybridization and highly sensitive bioelectronic protocols for detecting proteins and DNA were described based on the coupling of several CNT-derived amplification processes [112,131,132]. Further, reproducible and sensitive label-free DNA hybridization detection was also achieved with disposable MWNTs-modified graphite pencil electrodes based on the enhancement of

guanine signal using differential pulse voltammetry [128]. Chitosan films doped with CNTs onto graphite electrodes were used to detect salmon sperm DNA. Electrochemical detection of DNA hybridization has been accomplished using a paste electrode assembled by MWNTs and immobilizing DNA probe within electropolymerized polypyrrole (PPy) [133,134]. The detection approach is based on the significant changes in the current signal arising from the intercalation of ethidium bromide (EB) after DNA hybridization. Only the complementary DNA sequence gave an obvious current signal compared with the five-point mismatched and non-complementary sequences. The EB oxidation peak current was linearly related to the logarithm of the concentration of the complementary DNA sequence [134].

MWNTs and Pd nanoparticles were used to construct a sensitivity-enhanced DNA biosensor and were dispersed in Nafion, which were used to modify a GCE. The ability of CNTs to promote electron transfer and the high catalytic activity of Pd nanoparticles for the electrochemical reaction of methylene blue allowed a detection limit for target DNA of 1.2×10^{-13} M [135]. Recently, Ly et. al [136] have developed a non-treated blood assay and fast diagnosis method for detection of hepatitis B virus (HBV) using CNT sensor whose mechanical [137] and catalytic [138] properties are specific in this bioassay [139]. It was reported that the DNA was linked by paste on its surface [140] which sensitively responded to the analytical target proving its usefulness in the bio-sensing electrode. Here, novel HBV bioassay was developed using a bovine IgG immobilized onto a DNA-linked CNT sensor for bovine IgG–DNA–CNT linking bio-electrode. The bovine IgG was immobilized onto a DNA-linked CNT electrode sensor and monitored by square wave (SW) stripping and scanning by cyclic voltammetry (CV). The analytical parameters can be optimized and based on the method achieved in terms of low detection ranges for the HBV target, the developed methods can be used in direct assay of non-treated blood sera. This can also be applicable in organ monitoring, *in vivo* diagnosis, and other materials requiring HBV detection.

2.2. Carbon nanotube-based gas sensors

Recently, several groups reported that CNT could be used as a miniature chemical sensor [67,141]. Kong et al. demonstrated that the conductance of semiconducting SWNT (S-SWNT) could be substantially increased or decreased upon exposure to gaseous molecules, such as NO₂ or NH₃ [11]. The presence of gas molecules could be

determined by monitoring the electrical resistivities of nanotubes. The individual S-SWNT sensors were very small and had good sensitivity as high as 10^3 at room temperature. The nanotube sensors have shown to several have advantages over presently available metal oxide and polymer sensors. The reversibility of the nanotube sensor could be achieved by slow recovery under ambient conditions or by heating at a high temperature. In another study, Kong and Dai have reported that the decorating SWNTs with Pd nanoparticles can be used as molecular hydrogen sensors [12]. The Pd modified SWNT exhibited significant modulation of electrical conductance upon exposure to small concentrations of H_2 in air. The sensors were high sensitivity and reversible with fast response. Collins's group reported that the isolated semiconducting SWNT could be converted into apparent metals through exposure to oxygen at the room temperature [13].

Oxygen-saturated SWNTs had a higher electrical conductance than that with less adsorbed oxygen. Changes of DC electrical resistance or thermoelectric power of SWNT in different environments indicated that SWNT could be made as a sensitive oxygen sensor. It was demonstrated recently that a thermoelectric "nano-nose" could be built from tangled bundles of SWNTs [142]. The response was specific and gases such as He, N_2 , H_2 could be easily detected. Experiments showed the thermoelectric power and resistivity of a bundle of SWNTs varied with different gases, such as He, N_2 , H_2 , O_2 or NH_3 .

In the design of gas sensors, some unusual electronic, mechanical and thermal properties of CNTs are utilized and the unique feature characteristics of most reported sensing transduction modes related to conjugated polymers and carbon nanotubes have previously discussed [143]. The sensors developed so far have used different mechanisms of interacting analytes with CNTs, as well as different modes of preparing CNTs in sensors. For constructing gas sensors, most often, changes in the electrical properties of CNTs as result of their interaction with analytes are used. Changes in the resistance of the CNT layer have been used for detection of nitrogen dioxide [144–147], ammonia [147,148], hydrogen [148], and inorganic vapors in general [149]. Polymers have been used to impart high sensitivity and selectivity in sensors with chemical vapour deposition (CVD)-produced CNTs arranged across prefabricated electrode arrays [147]. NO_2 was detected without interference by NH_3 with polyethyleneimine coating, while, selective sensing of NH_3 was observed with Nafion coatings (Fig. 3). It was shown that the deposition of poly(o-anisidine) onto CNTs imparted higher sensitivity in detecting

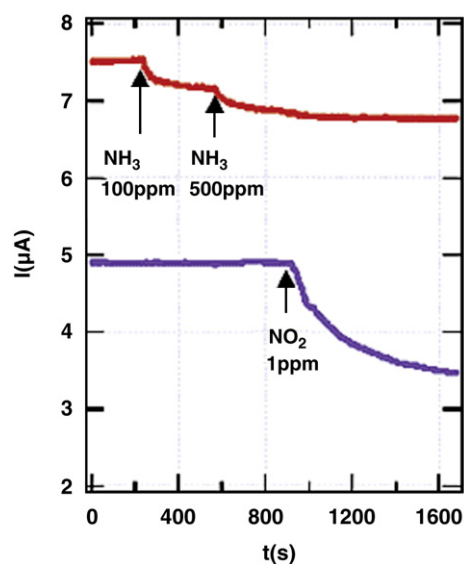


Fig. 3. Response curves recorded for gas sensor comprising multiple SWNTs functionalized with Nafion for NH_3 sensitivity and with polyethyleneimine coating for NO_2 [147].

inorganic vapor, which was attributed to direct charge transfer with electron hopping affecting intertube conductivity through physically adsorbed polymers [149]. The detection of carbon monoxide with sensors based on MWNTs was shown to occur by strong catalytic effect toward the electrochemical oxidation of CO [150]. A MWNT sensor fabricated on silicon wafer exhibited Schottky behavior with marked sensitivity or current changes in the presence of hydrogen [151]. Increasing detection sensitivity in hydrogen sensing was observed with increasing operating temperature.

MWNTs have been employed for monitoring changes of electrode impedance as analytical signal for detection. NH_3 was detected with CNTs trapped in an interdigitated microelectrode gap [152]. Increasing impedance was observed also for MWNT sensors with increasing humidity or partial pressure of NH_3 , CO and CO_2 [153]. Humidity sensing was also reported using Nafion-coated SWNT field-effect transistors (FETs) [154] and sensors with carboxylated MWNTs modified with lithium perchlorate [155]. For studying the gas-sensing properties of CNTs, a circular disk resonator was also employed to detect the presence of gases based on changes in the dielectric constant rather than the electrical conductivity [156]. Noticeable shifts in resonant frequency to both polar (NH_3 , CO) and non-polar gases (He, Ar, N_2 , O_2) were observed.

The sorption properties of CNTs can be utilized in piezoelectric detection of volatile analytes. Ammonia was detected with sensors comprising a circular disk of electromagnetic resonant circuit coated with CNT, which upon exposure to NH_3 , the electrical resonant frequency exhibits a dramatic downshift [157]. The recovery and response times were within 10 min. Composite humidity-sensing films have been made from CNTs and Nafion on the electrode of a quartz crystal microbalance (QCM) [158]. For piezoelectric detection of alcohol vapor, a QCM electrode was covered with Langmuir-Blodgett films comprising tangled bundles of SWNTs without surfactant [159]. The same work, for the same purpose, also reported on a refractive index-sensitive silica optical fiber deposited with SWNTs. Volatile organic compounds (VOCs) can be detected with surface acoustic wave (SAW) sensors with CNT deposited onto quartz substrates [160]. The selectivity of response can be controlled by the type of organic solvent used to disperse CNTs on the sensing surface of the sensor. The thermoelectric properties of SWNTs are sensitive to gases in contact with the tube walls. The contact of SWNTs with He, N_2 and H_2 can easily be detectable and the resulting thermoelectric power change is shown to be reversible [161]. Small polar alcohol molecules give a large thermoelectric response, while water has no effect. Gas-ionization microsensors have also been reported and shown the electrical breakdown of a range of gases and gas mixtures at CNT tips [162]. The sharp tip of CNTs generate high electric fields at relatively low voltage that lowers breakdown in voltages and enabling operation of such microsensors to be battery-powered.

Kang et al. have developed a novel microelectronic gas sensor utilizing CNTs for hydrogen detection (Fig. 4). MWNTs were grown on Si substrate by thermal CVD at atmospheric pressure using palladium (Pd) as a catalysts [163].

The sensitivity of CNTs to hydrogen gas was measured as a function of hydrogen gas partial pressure at several temperatures. SEM micrograph of CNTs (Fig. 5) shows that the CNTs grown were highly dense with diameter ranging from 40 to 60 nm. The I - V characteristics of the sensor (Fig. 6) exhibit diode behavior at room temperature with drastic current changes in the presence of hydrogen [163]. The successful utilization of carbon nanotubes in gas sensors may open a new door for the development of superior nanoelectronic gas sensors.

Microwave plasma etching and Pd decoration methods were employed for the modification of CNTs [164]. The defects on the nanotube wall increased after the etching process and these defects allows access to more hydrogen supplied to the interlayers and hollow interiors of CNTs. The results of hydrogen uptake measurements

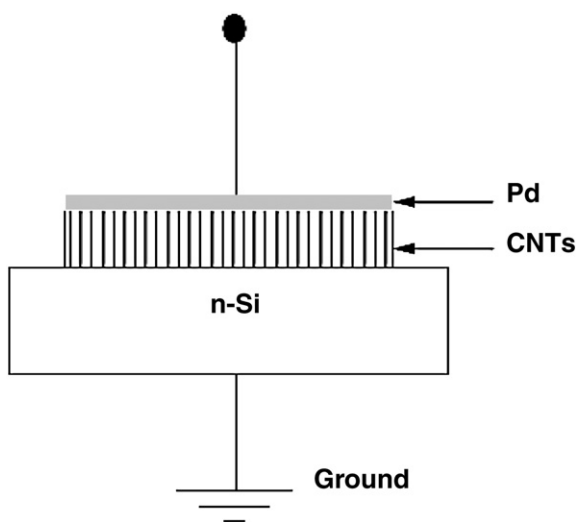


Fig. 4. Schematic Structure of CNTs sensor, with permission [163].

showed that the etched CNTs had higher hydrogen storage capability than that of the original sample at ambient temperature and pressure of 10.728 MPa. Furthermore, the CNTs decorated with Pd showed a hydrogen storage capability of 4.5 wt.%, which is about three times higher than that of the non-decorated samples. The hydrogen uptake mechanism of the modified CNT has been previously discussed. For example, Consales et al. reported the performance analysis of silica optical fiber (SOF) and QCM coated by SWNTs multilayers and used as volatile organic compounds (VOCs) sensors for detection of toluene and xylene vapors at room temperature [165]. The results obtained from VOCs sensor have been demonstrated to have good sensitivity, fast response and high repeatability even at very low concentrations.

Santhosh et al. has reported a novel amperometric sensor based on MWNT grafted polydiphenylamine (PDPA), termed as MWNT-g-PDPA developed for the determination of carbon monoxide (CO). The dependence of the response current on CO concentration is explored and under optimal conditions, an excellent linear concentration range with a substantially low detection limit between 10 and 200 ppm is reported [166].

Balazsi et al. fabricated novel hexagonal WO_3 nanopowder decorated CNTs as NO_2 gas sensor [167]. Metallic nanoclusters (Ag, Au) were added to the CNTs for improving the gas sensing properties

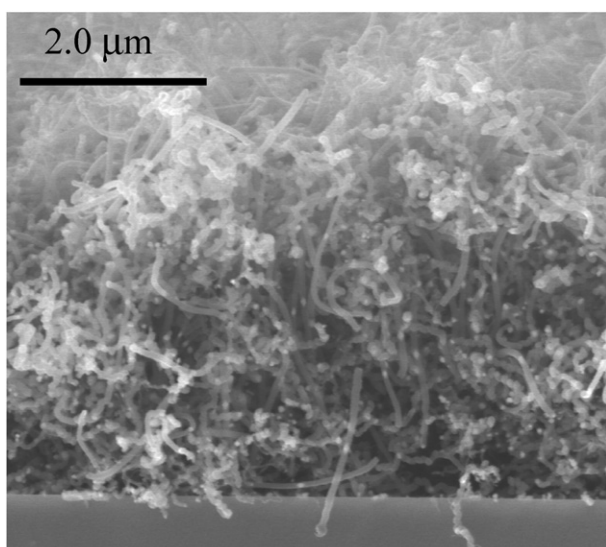


Fig. 5. SEM of CNTs, with permission from [163].

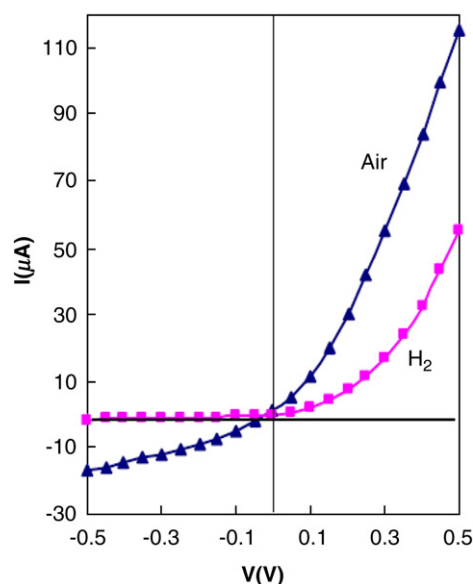


Fig. 6. Characteristics of CNTs gas sensor (I - V) [163].

of the films. The addition of MWNTs lowered the temperature range sensitivity of the hex- WO_3 nanocomposites to NO_2 hazardous gas. In comparison, the sensitivity of hex- WO_3 to NO_2 was in the temperature range between 150 °C and 250 °C, while the hex- WO_3 /MWNTs composites were sensitive to NO_2 gas at room temperature.

Penza et al. developed a gas chemiresistor fabricated onto alumina using MWNTs networked films grown by radiofrequency plasma enhanced chemical vapor deposition (RF-PECVD) technology for high-performance gas detection at 200 °C [168]. Functionalization of MWNTs tangled bundle-films with nominally 5-nm thick Pt- and Pd-nanoclusters has been prepared by magnetron sputtering. It provided higher sensitivity for significantly enhanced NO_2 , H_2S , NH_3 , CO, gas detection at sub-ppm levels. The measured electrical conductance of the functionalized MWNTs upon gas exposures is modulated by charge transfer with p-type semiconducting characteristics. Pt and Pd-nanocluster functionalized MWNT gas sensors exhibited better performances compared to unfunctionalized MWCNTs, making them promising candidates for air-pollutants for environmental monitoring. Simple electronic interface for the chemiresistor has been developed with a voltage output of the sensor signal.

3. Diamond for chemical sensing

3.1. Diamond microelectrode for electrochemical sensing

Currently, extensive quests are on going for development of high throughput systems by using proper transducer materials for optimization of detection techniques as well as sensitivities, realization of highly integrated sensor arrays, and bio-interfaces that show high chemical stability. Genomics research has elucidated many new biomarkers that have the potential to greatly improve disease diagnostics [169–171]. The availability of multiple biomarkers is important in the diagnosis of complex diseases like cancer [172,173]. In addition, different markers will be required to identify different stages of disease pathogenesis to facilitate early detection. The use of multiple markers in healthcare will, however, ultimately depend upon the development of detection techniques that will allow rapid detection of many markers with high selectivity and sensitivity. Most of the established substrate materials ('transducers') like latex beads, polystyrene, carbon electrodes, gold and oxidized silicon or glass do not possess all the desired properties like flatness,

homogeneity, chemical stability, reproducibility and biochemical surface modifications [38,40,41,174,175]. In addition, future technologies require integration of bio-functionalized surfaces with microelectronics or micromechanical tools, which adds significant complexity to this topic [38,39,176–178]. Most microelectronic-compatible materials like silicon, SiO_x and gold show degradation of their bio-interfaces in electrolyte solutions [39].

Diamond is a promising material for biochemical applications, because of its durability, chemical inertness and its carbon composition, which is the basis of all organic matter. The high strength of C–C bonds as well as the established biocompatibility makes diamond a particularly attractive substrate for biosensor applications [179]. Efforts were therefore made in the past to functionalize diamond surfaces [180–182]. Nevertheless, economic considerations and a lack of information have prevented a clear judgment of the potential of diamond in this particular field. The advent of a new diamond thin-film deposition technology [183] and recent breakthroughs in substitutional doping of diamond [184,185] have generated renewed interest. Indeed, the possibility of depositing large-area thin films of NCD on diverse substrates at a relatively low cost. Moreover, the NCD has nearly the same combination of exceptional properties as single-crystal diamond, such as biocompatibility, chemical inertness and superb electrochemical properties [186] that quickly led to considerable progress [39,187]. Yang et al. have demonstrated the modification of NCD surfaces with DNA oligonucleotides and shown that NCD as a substrate for DNA immobilization has superior properties to those of other materials such as glass, gold or silicon [179]. Diamond as an active substrate interacting with biomolecules immobilized on it has a potential that goes beyond a passive role as a substrate for anchoring biomolecules. This is because of the following reasons; (a) its low background current, (b) large electrochemical potential window as an electrode [188], (c) fouling resistance and chemical inertness together with the presence of a quasi-two-dimensional conductive layer at the surface of hydrogen terminated diamond [189–191].

Diamond can become a promising candidate for bioelectronics as it shows good electronic [192–194] and chemical properties [36,44,45]. Granger et al. [195,196] studied voltammograms for water electrolysis of various electrodes. The supporting electrolyte was 0.5 M H₂SO₄. It was reported that each current/voltage scan has been shifted vertically for better comparison [197]. The electrochemical potential window of diamond is significantly larger and the background current within this regime considerably lower than that found with conventional materials. In addition, by tuning the boron-doping level, the onset of hydrogen evolution can be reduced or switched off completely by decreasing the boron-doping level from extremely high (>10²⁰ cm⁻³) metallic boron to ‘undoped’ (intrinsic diamond). There are some other parameters affecting the electrochemical potential window like crystal orientation [198], structural perfection of polycrystalline diamond [199] and surface termination [182].

Surface induced conductivity of hydrogen-terminated undoped diamond in electrolyte solutions is another unique property which has attracted significant attention in recent years [189]. The conductivity is generated by transfer doping of hydrogen-terminated diamond immersed into electrolyte solution. The phrase ‘transfer doping’ indicates that the surface conductivity in diamond arises from missing valence-band electrons as such electrons ‘transfer’ into the electrolyte [190,200,201]. For such transitions, the chemical potential of an electrolyte must be below the energy level of the maximum valence-band. For most semiconductors this is not the case, even for oxidized diamond, chemical potentials are mostly deep in the band-gap of diamond [190]. It changes drastically if the surface of diamond, consisting of about 2 × 10¹⁵ cm⁻² carbon bonds is terminated with hydrogen. Hydrogen–carbon bonds are polar covalent bonds. Therefore a dense surface dipole layer is generated with slightly negative charged carbon (C⁻) and slightly positive charged hydrogen (H⁺). From basic electrostatic forces, a dipole layer causes an electrostatic

step potential ΔV is generated perpendicular to the surface over a distance of the order of the C–H bond length of 1.1 Å. Simple calculations show that the energy variation over this dipole is in the range of 1.6 eV (for a detailed discussion see [202]). This dipole energy shifts all energy levels of diamond about 1.6 eV up with respect to the chemical potential of an electrolyte. Conduction band states of diamond are shifted above the vacuum level of the electrolyte. This scenario is called ‘negative electron affinity’.

In case of clean diamond, the vacuum level is about 0.3 eV above the conduction band minimum. Whereas in H-terminated diamond, the vacuum level is 1.3 eV below the minimum conduction band [190,203]. Occupied valence-band states emerge above the chemical potential μ of electrolytes as all electronic states are shifted by the same dipole energy. Electrons from the diamond valence-band (electronically occupied states) can therefore tunnel into empty electronic states of the electrolyte, until thermodynamic equilibrium between the Fermi level of diamond and the electrochemical potential of the electrolyte is established. Fermi-level and chemical potential, μ, align and form a narrow valence-band bending of 20–30 Å in width, which forms a confined hole accumulation layer [204,205]. Such alignment requires defect free bulk and surface properties and a perfect H-termination. During recent years, the growth of diamond has been optimized to such a level in combination with a perfect H-termination of the surface (for reviews see [206,207]). Evidence from theory and experiments suggests that the electron affinity of diamond in contact with water is approximately 1 eV more positive than that observed in high vacuum [208–210]. A dominant interaction of diamond energy levels with the H₂/H⁺ redox states therefore seems to be less likely. But diamond valence-band states will still scale up with interactions to the O₂/H₂O couple giving rise to the discovered phenomena. As the chemical potential of electrolytes change with pH-value, a variation of the surface conductivity can be experimentally detected, closely following the Nernst prediction with 55 mV/pH [211–213].

Diamond is known to be biocompatible [50,214,215] and therefore has a potential for ‘in vivo’ electronic applications. A giant step towards bio-functionalization of diamond was taken, as the obstacle of ‘chemical inertness’ of diamond had finally been removed. Takahashi et al in 2000 [216,217] first introduced a photochemical chlorination/amination/carboxylation process of the initial H-terminated diamond surface. This triggered more activities so that two years later, Yang and co-workers in 2002 introduced a new photochemical method to modify nano-crystalline diamond surfaces using alkenes [39]. This was followed by electrochemical reduction of diazonium salts which has been successfully applied to functionalize boron-doped ultra-nano-crystalline diamond [218]. Recently, a direct amination of diamond has been introduced [219]. Such functionalized surfaces have been further modified with DNA, enzymes and proteins and characterized using fluorescence microscopy, impedance spectroscopy [39,220,221], voltammetry, and gate-potential shifts of ion-sensitive field-effect transistors (ISFETs) [179,222].

Diamond electrodes of various designs, such as planar and patterned microstructural array of diamond were fabricated by Kang et al. [163]. The fabrication of micropatterned structural electrodes was performed via a mold transfer technique [163]. Various geometrical structures of diamond microelectrode arrays, such as microtips, microdiscs, and microbands have been designed and fabricated by chemical vapor deposition of diamond combined with *in situ* gas phase doping method. Further, Kang et al. also developed diamond microelectrode for electrochemical sensing. Fig. 7 shows a scanning electron micrograph of a boron-doped diamond planar electrode [163]. It can be seen that the surface of the planar diamond film is well-faceted with nominal crystallite size from 2.2 μm to 2.4 μm. Fig. 8 shows the SEM micrograph of a micropatterned electrodes with pyramidal tips array [163]. These micropatterned electrodes with pyramidal tips array have a tip base of 2 μm × 2 μm and an ultra sharp

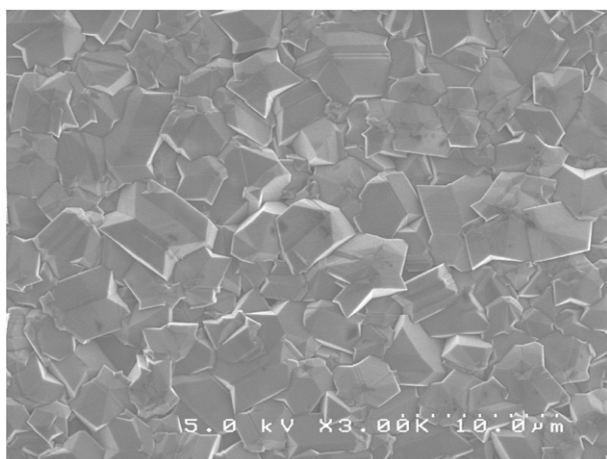


Fig. 7. SEM of boron-doped diamond planar electrode, with permission from [163].

diamond tip radius of curvature of ~ 5 nm. The molding process developed for the fabrication of the diamond tips electrode is a practical technique to create well-controlled and uniform microstructures suitable for a number of electrochemical applications.

For electrochemical studies, the diamond electrode was initially cycled in background electrolyte solution giving a working potential window from -1.5 V to $+1.3$ V versus a Ag/AgCl reference electrode, as shown in curve (b) of Fig. 9 [163]. This large 2.8 V potential window in aqueous KCl electrolyte demonstrated the non-catalytic behavior of the diamond surface for either water oxidation or reduction. The diamond electrode was then tested for detection of 1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ in 0.1 M KCl. The electrode showed quasi-reversible kinetics as apparent from the narrow peak separation as seen in curve (a) of Fig. 9 [163]. The peak-to-peak separation (ΔE_p) is 180 mV, indicating a quasi-reversible redox reaction at the electrode. Typically, cyclic voltammetry of ferrocyanide at a metal electrode would have ΔE_p that approaches 60 mV. The diamond electrode obtained a reversal peak current ratio, $I_{p,\text{red}}/I_{p,\text{ox}}$, of ~ 0.8 which approaches the limit for a reversible electron transfer of 1.0, which is the ideal reversible behavior of a fully conductive electrode that might be expected in the voltammetry of dilute ferrocyanide.

Fig. 10 shows the CV using the diamond film for detection of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.5 M KCl at four different scan rates (10, 50, 100 and 500 mV/s). The $\text{Fe}(\text{CN})_6^{4-/3-}$ redox reaction at the diamond electrode exhibits quasi-reversible electrochemical kinetics [163]. The position of the oxidation peak potential ($E_{p/\text{ox}}$) in the forward sweep shifts slightly to the right with each increasing scan rate as does the peak

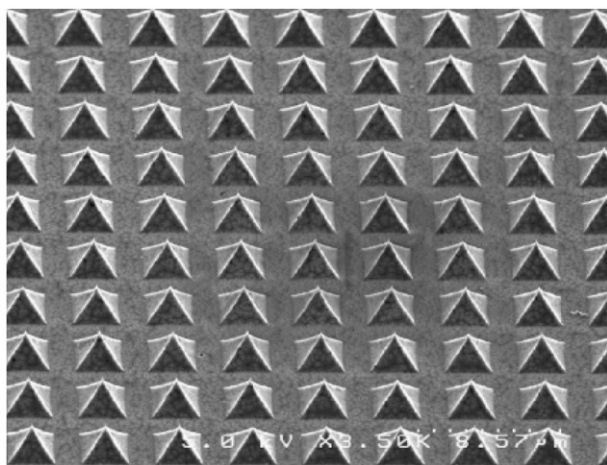


Fig. 8. SEM of a micropatterned pyramidal diamond tips array, with permission from [163].

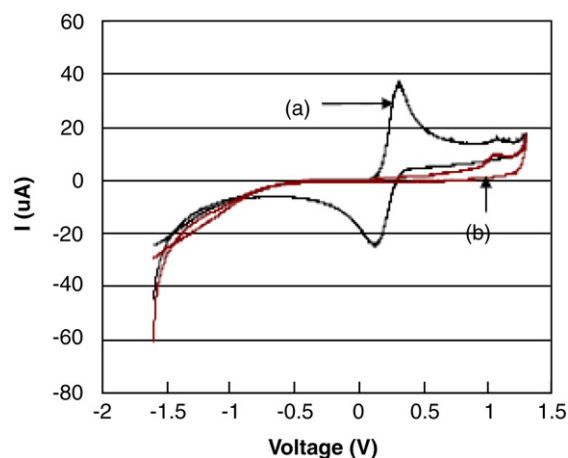


Fig. 9. Cyclic voltammogram of boron-doped diamond planar electrode [163]: 1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ in 0.1 M KCl, (b) 0.1 M KCl. Scan Rate = 50 mV/s.

separation, ΔE_p , indicating that the $\text{Fe}(\text{CN})_6^{4-/3-}$ redox reaction at the electrode is kinetically limited. A graph of oxidation peak current versus the square root of scan rate is linear for scan rates between 0.1 V/s and 0.01 V/s suggesting a redox process as expected for an inert diamond surface. All of the reversal peak current ratios approach 1.0 which indicates both ferrocyanide and ferricyanide were stable in solution and exhibited similar electron transfer kinetics. The diamond planar electrode was also tested for sensitivity and linearity for the electroanalytical detection of various analyte concentrations. Fig. 11 shows detection of $\text{Fe}(\text{CN})_6^{4-}$ in a concentration range of 0.5 mM to 5.9 mM. When the oxidation peak current is examined as a function of the $\text{Fe}(\text{CN})_6^{4-}$ concentration, a linear response is obtained and it was observed that the position of $E_{p/\text{ox}}$ is independent of the analyte concentration for an outer-sphere electron transfer [163].

Likewise, the diamond pyramidal microtip array electrode was tested for detection of $\text{Fe}(\text{CN})_6^{4-}$ [163]. Fig. 12 shows that the pyramidal microtip array electrode was capable of picking up higher oxidation current for the same concentration of analyte. This increase in sensitivity can be attributed to an overall increase in electrode surface area and also possibly due to enhanced mass transport at the microtip region as compared to the planar electrode. The sensitivity of the microarray electrode was about twice that of the planar film, and both films displayed a linear response [163].

In contrast to the molded growth, the postgrowth etching was found to be another approach to structuring diamond films. Nanostructured diamond honeycomb films were constructed by etching in oxygen plasma through a porous anodic alumina etching mask [223]. High aspect ratio diamond nanocone arrays were formed

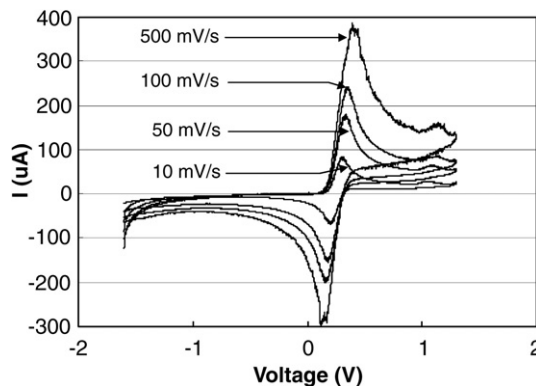


Fig. 10. Cyclic voltammogram of boron-doped diamond planar electrode for detection of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.5 M KCl, scan rate = 500 mV/s, 100 mV/s, 50 mV/s and 10 mV/s, with permission from [163].

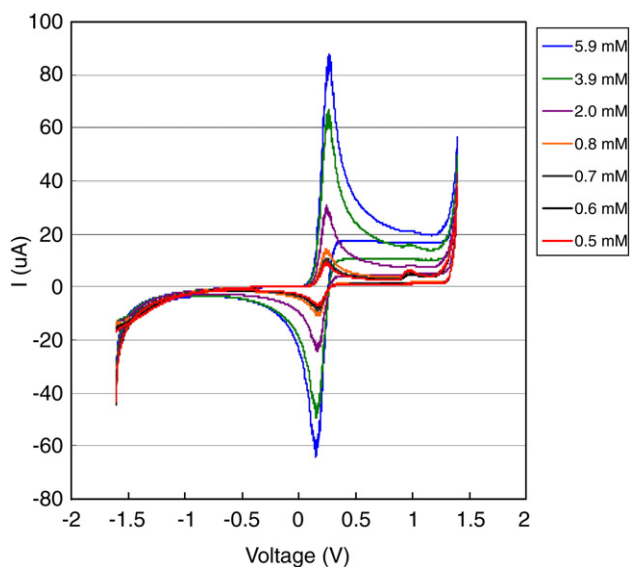


Fig. 11. Cyclic voltammogram of boron-doped diamond planar electrode for detection of various concentration of $\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M KCl. Scan rate = 10 mV/s, with permission from [163].

on freestanding diamond films by focused ion beam (FIB) milling [224]. Reactive ion etching (RIE) has also been revealed to be a low-cost but effective method to construct diamond films [225–230]. Single-crystalline [001]-oriented and nanocrystalline diamond cone arrays were fabricated by using an *in situ* bias-assisted RIE [225–228]. Diamond nanopillars (also termed as nanorods or nanowhiskers) have been fabricated by top-down methods, including RIE with or without mask, FIB milling and bottom-up approaches [231,232]. Polycrystalline diamond films formed by air plasma etching resulted in a network-like pattern of diamond nanowhiskers with poor uniformity [233]. Monocrystalline diamond nanorods were fabricated by etching high-pressure, high-temperature single crystal diamond wafers with oxide or Al dot mask [234]. Well-aligned polycrystalline diamond cylinder (diameter ~300 nm) arrays were also grown with the assistance of anodic porous alumina mold [235]. For the practical applications of diamond nanostructures, it is still of great interest to develop a low-cost, versatile, and applicable method to obtain diamond nanostructures with high areal density, uniformity, and controlled geometry.

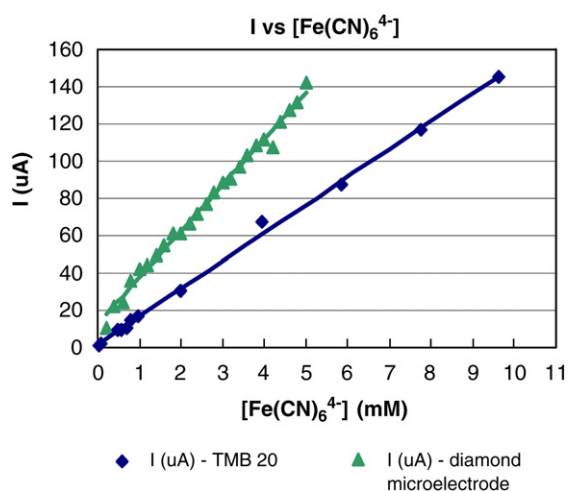


Fig. 12. Graph of oxidation current, I (μA) versus concentration of $\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M KCl: (a) boron-doped diamond planar electrode, (b) patterned diamond pyramidal microarray. Scan rate = 10 mV/s [163].

The potential applications of materials depend not only on its intrinsic properties, but also on the surface geometries in which they appear. Surface nanostructuring is known to be an effective approach to extend and/or enhance the properties of materials with respect to their bulk and film counterparts. As an example in diamond applications, it has been demonstrated that diamond coatings on silicon tip arrays drastically reduce the turn-on field electron emission (FEE) [236]. However, the extreme hardness and chemical inertness of diamond makes it difficult to be structured to a desired geometry. So far, considerable effort has been made to grow diamond in different structures. For example, polycrystalline diamond pyramids made by a molding technique have been used in scanning probe microscopes [237].

A field-effect capacitive EDIS structure has been introduced as a platform for (bio-) chemical sensing [238]. In contrast to transistor structures, EDIS sensors are simple in layout and cost-effective in fabrication. Usually, no photolithographic process steps or complicated encapsulation procedures are required for the capacitive field-effect EDIS structure. In addition, alternating current (AC) measurements with the EDIS structure are often more informative than static direct current (DC) measurements. A feasibility of this platform has been demonstrated by realising a pH-sensitive EDIS sensor with NCD films [238].

Recently, the feasibility of a capacitive field-effect EDIS platform for multi-parameter sensing has been reported [239]. Here, EDIS sensors was developed with an O-terminated NCD film as transducer material for the detection of pH, penicillin concentration and the label-free electrical monitoring adsorption and binding of charged macromolecules, like polyelectrolytes. The NCD films were grown on *p*-Si-SiO₂ substrates by microwave plasma-enhanced chemical vapour deposition. The NCD-based field-effect sensors have been characterised by means of constant-capacitance method. The average pH sensitivity of the O-terminated NCD film was 40 mV/pH. EDIS penicillin biosensor immobilised with penicillinase enzyme showed high sensitivity toward penicillin G (65–70 mV/decade) with a low detection limit (5 μM) [239].

Nebel et al. introduced a new concept towards a novel bio-sensing platform by combination of a) geometrically controlled DNA bonding using vertically aligned diamond nano-wires and b) the superior electrochemical sensing properties of diamond as transducer material [240]. Ultra-hard vertically aligned diamond nano-wires are electrochemically modified to bond phenyl linker-molecules on their tips which provide mesospacing for DNA molecules on the transducer. The nano-wires are generated by reactive ion etching of metallic boron doped single crystalline CVD diamond. Further, the authors also reported the properties of electro- and bio-chemical sensor using cyclic and differential pulse voltammetry as well as impedance spectroscopy with $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox mediators.

These sensors showed sensitivities to 2 pM concentration on 3 mm² sensor areas and superior DNA bonding stability over 30 hybridization/denaturation cycles. The fabrication of “all diamond” ultra-micro-electrode (UME) arrays and multi-gene sensors are discussed taking into account the unique properties of diamond. This research group have introduced a technological pathway for device miniaturization using “diamond only” as approach to maintain the major advantages of diamond like hardness, chemical stability and biocompatibility for sensing. Diamond nano-wires can resist in harsh environments unlike other materials, such as ZnO₂, SnO₂ and Si wires. Biosensors from diamond can be renewed after deterioration of sensitivity, simply by application of a new cycle of chemical cleaning and chemical functionalization without going through a full solid-state sensor production. Such robust devices perfectly suit for the demand in high through-put systems of clinical environments.

Enzyme-based electrochemical biosensors have been around for many years, involving many different types of enzymes, immobilization chemistries and substrates. Indeed, glucose sensors (used by

millions who suffer from diabetes) work using this principle, and the covalent immobilization of glucose oxidase or similar enzymes on relatively inexpensive materials already forms the basis for commercial devices. Therefore, at a first glance, the immobilization of the enzyme catalase on diamond reported by Jose Garrido et al., may not seem particularly original [191]. Yet, this result may dramatically alter the landscape in this area. Recent advances in the synthesis of highly conducting nanocrystalline-diamond thin films, as well as the development of new chemical approaches to anchor biomolecules covalently to these surfaces may lead to an entirely new class of electrochemical biosensors and bio-inorganic interfaces. Diamond is well known for its exceptional hardness, thermal conductivity and high index of refraction. But there are several lesser-known surface properties that potentially make diamond an interesting platform for biosensors and bio-interfaces. For instance, the chemical inertness of diamond makes it suitable for most biological environments. The surface of most diamond thin films is terminated with hydrogen-carbon bonds that are very stable and resistant to chemical attack. In addition, conducting diamond films have superior electrochemical properties [186]. The voltages that can be applied to a diamond based electrode without triggering hydrolysis (the production of H₂ or O₂ molecules from water) are very large (about ± 2.5 V). This means that diamond surfaces can be used to study redox reactions in aqueous media with a high degree of sensitivity compared with other electrode materials, including those selectively triggered by enzymes within this 'voltage window' that is unique to diamond.

Making synthetic diamond thin films that are conducting enough to be electrochemically active at room temperature has been always difficult. P-type doping (conduction occurs through holes) turned out to be relatively easy but n-type doping (conduction occurs through electrons) has remained an elusive goal until recently. NCD thin films consisting of diamond grains of nanometers in size can be made highly n-type conductive at room temperature. This can be accomplished through the addition of nitrogen gas to the microwave plasma used to grow these materials [241]. Nitrogen atoms are thought to be incorporated into the narrow boundaries between the grains leading to enhanced electron transport. These n-type NCD films, which are not semiconductors but are in fact semimetallic in nature, have conductivities as high as 250 Ω⁻¹cm⁻¹ at room-temperature. However, the surface chemistry and electrochemical properties are still essentially equivalent to those of normal diamond [242].

Having conducting films and the potential for diamond-based electrochemical interfaces is one thing. But the challenge comes in covalently linking organic molecules to surfaces that are normally chemically inert. The realization of this potential has come over the last two years in two separate reports, both published in *Nature Materials*. The first breakthrough came in 2002, when Hamers' group demonstrated that an amine terminated hydrocarbon chain could be attached to the surface of nanocrystalline diamond through a photochemical process [243]. This new immobilization strategy was then used to covalently link short synthetic DNA sequences. Compared with benchmark silicon and gold surfaces that are more commonly used to immobilize probe molecules, diamond gives an extraordinary stability of the attachment as a consequence of the high stability of the C-C bond that links the surface to the amine terminated hydrocarbon. Whereas the work of Hamers' group focused on synthetic DNA fragments, the covalent attachment of proteins reported by Garrido and colleagues is an order of magnitude more challenging because proteins are larger and much more delicate molecules than DNA fragments. This demonstrates that the same immobilization chemistry developed by Hamers and colleagues could be applied to attach an enzyme to a diamond surface. By doing so in a way that preserves its functionality is a remarkable feat in itself. But the authors have gone even further and demonstrated the ability of the diamond surface to electrochemically drive and detect redox reactions of immobilized enzyme catalysis [191].

Considering the recent advances in diamond thin film synthesis, materials integration and diamond microfabrication [244], the latest results published here bring us close to the realization of protein-based biosensors with unprecedented sensitivity and stability. For example, an implanted real time glucose sensor that monitors the blood-sugar level from a suspected individual with diabetes. NCD based electrodes provides a grand challenge of a true electrochemical bridge between the organic and inorganic worlds that is being investigated at the Argonne National Laboratory. This group is attempting to communicate electrochemically with membrane proteins integrated into artificial lipid bilayers on nanocrystalline-diamond surfaces. Moreover, biosensors that use both gravimetric and electrochemical forms of transduction could be developed using diamond films that are compatible with silicon-based electronics [245,246]. Abouzar's group demonstrated the feasibility of a capacitive field-effect EDIS platform for multi-parameter sensing [239,240] and developed EDIS sensors with an O-terminated NCD film as transducer material for the detection of pH and penicillin concentration as well as for the label-free electrical monitoring of adsorption and binding of charged macromolecules, like polyelectrolytes.

Nano-wires are new materials, which have characteristics with sometimes extraordinary mechanical, electrical, thermal and multi-functional properties [247,248]. The properties of nano-wires can be used for tunable transport of electrons. The electronic properties of these nano-wires are strongly influenced by small perturbations on the surface and surface-to-volume ratio for enhanced chemical/bio-chemical applications. Nano-wires are generated by a) self-assembly of small sized structures to form larger structures (bottom up) or b) by reduction of large systems down to small size (top-down) [249-251]. The nano-wire structures need to offer advantages over CNTs for bio-sensing devices. These include, a) diamond properties be controlled by tuning conditions for synthesis (dimension and morphology), b) conductivity be controlled by doping, which allows fabrication of insulating, semiconducting, and metallic wires, and c) the surface of nano-wires be functionalized by use of well established chemistries [102,252-255]. As described before, H-terminated diamond surfaces are hydrophobic while O-terminated surfaces are hydrophilic in nature. Diamond is ultra-hard (50-150 GPa) which is promising with respect to mechanical stability of diamond nano-wires [256].

The realization of diamond nano-wires started in 1997 by Shiomi [257] and demonstrated the formation of porous diamond films by RIE using O₂. Later in 2000, nanostructured diamond honeycomb films have been prepared by etching through a porous anodic alumina mask [223], triggering some activities which are summarized in an article of Shenderova et al. [258]. Growth induced formation of nano-scale tubular structures have been reported for the first time in 2003, applying a microwave plasma of hydrogen under a bias potential [259]. Recently, in 2008, Zou et al. [260] reported on the fabrication of nanopillar arrays using self aligned Au nanodots as etching mask in a bias-assisted RIE by applying a hydrogen/argon plasma. Although these achievements demonstrate that vertically aligned diamond nano-wires can be fabricated by a variety of methods, no applications so far reported for application in electro- or bio-chemistry. Recently, Nebels' [240] group introduced nano-wires for controlled bonding of DNA molecules to diamond. This concept combines with the outstanding electrochemical properties of diamond as transducer through dispersed and controlled bonding of DNA molecules. The geometrical, electronic, optical and electrochemical properties of these wires need to be characterized in detail in the future. The reproducibility can be improved with respect to size and length of wires combined with chemical surface modification for gas- chemical- and bio-chemical sensing.

Research groups in Japan, the US and Europe are working towards the attachment of several biomolecules of interest, including amino acids, peptides and polynucleic acid sequences on diamond surfaces. But several challenges lie ahead including the need for new

immobilization chemistries that can be more efficient and flexible than the existing photochemical process. Diamond surfaces are naturally hydrophobic, so protein denaturation and the concomitant non-specific absorption of biomolecules needed to be addressed. In the not-so-distant future, we would see the realization of diamond-based electrochemical biosensors for applications ranging from microelectromechanical-based assays to gene-chips and proteomics. But these are just the first steps on a long road to practical devices.

3.2. Diamond based gas sensors

Kang et. al developed a microelectronic gas sensor utilizing polycrystalline diamond film in conjunction with a catalytic metal for hydrogen detection [261]. The sensor is fabricated in a layered Pd/i-diamond/p-diamond metal-insulator-semiconductor (MIS) with Schottky-diode configuration on a tungsten substrate. The performance of the sensor for H₂ detection has been examined in the temperature range 27 – 300 °C. The hydrogen adsorption process has shown to be due to the barrier-height change in the diamond-based MIS Schottky diode.

Gurbuz et. al utilized diamond as high temperature tolerant semiconductor in an MIS structure for the detection of hydrogen gas [262,263], CAIS (catalyst/absorptive-oxide/insulator/semiconductor) structure for the detection of oxygen [264,265] and CO [265–267]. In these sensors, the authors have utilized PECVD diamond technology in realization of novel microelectronic gas sensing structures. The advantages of using diamond in these sensors are; a) a promising semiconductor material for microelectronic device applications at higher and wider operating temperature range, b) it is immune to the corrosive environments due to its hardness coefficient and chemically inertness, c) the superior electrical and physical properties of diamond, radiation hardness, suitability for micropatterning, larger band gap, higher thermal breakdown voltage and thermal conductivity, and high hole mobility further enhances the utilization of diamond over Si and GaAs in microelectronic gas sensor applications. First structure incorporates a gas sensitive electrode (Pd) with diamond to form a diamond based MIS sensor for hydrogen gas detection (Fig. 13). The catalytic metal, Pd, has shown to be reacting with hydrogen, thus incorporating this metal with diamond in MIS device leads to the detection of hydrogen gas [163]. The major advantage of using diode-type structure here in this sensor is that any electrochemical change at the interface of catalytic metal-semiconductor diamond, such as ionization of hydrogen molecules/atoms, causes a change in the energy barrier of the device, hence resulting an exponential change in the device current. In other words, the diode structure enhances the detection signal and simplifies the need for a detection-signal processing/enhancing.

Typical *I-V* characteristics of the gas sensor before and after exposure to H₂ (concentration: 100%, flow rate: 10 ml/min) in open air are shown in Figs. 14 and 15 for two types of devices operating at

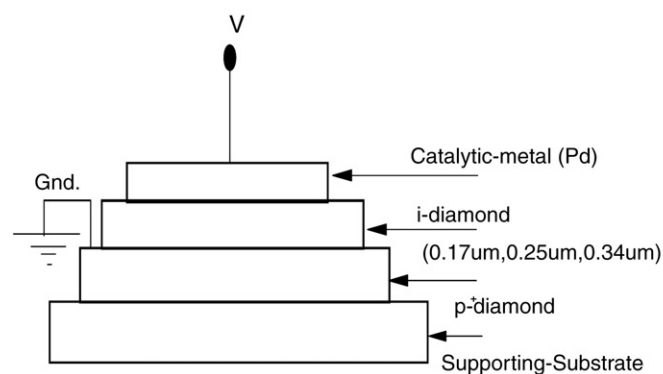


Fig. 13. A schematic of the prototype gas sensor [163].

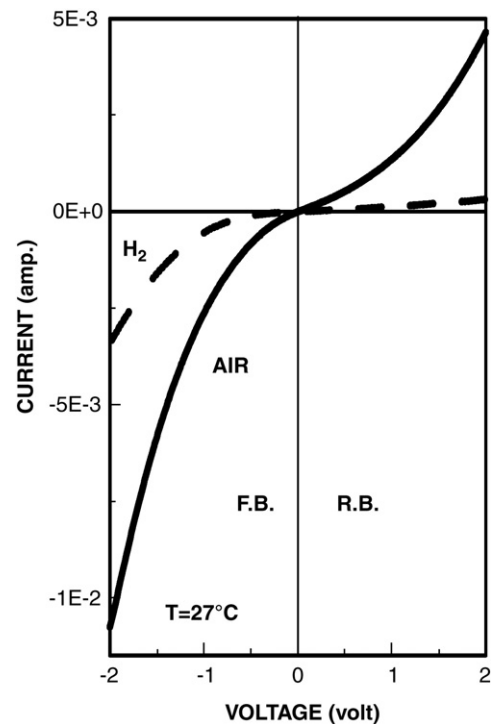


Fig. 14. *I-V* Characteristics of diamond-based H₂ sensor in air and H₂ environments at T=27 °C [163].

27 and 300 °C, respectively. The figures show the large change in the *I-V* characteristics of the sensor upon exposure to the H₂ gas. They also reported adsorption/desorption of hydrogen gas is reproducible [163].

The second structure utilizes a catalyst (Pt) in conjunction with an adsorptive oxide (SnO_x) to form a catalytic metal-adsorptive oxide-insulative diamond-semiconductor diamond (CAIS) of diode structure, enhancing gas sensitivity and selectivity (Fig. 16).

The sensitivity is extended towards oxidizing gases such as O₂ and reducing gases such as CO, and H₂ due to the utilization of adsorptive

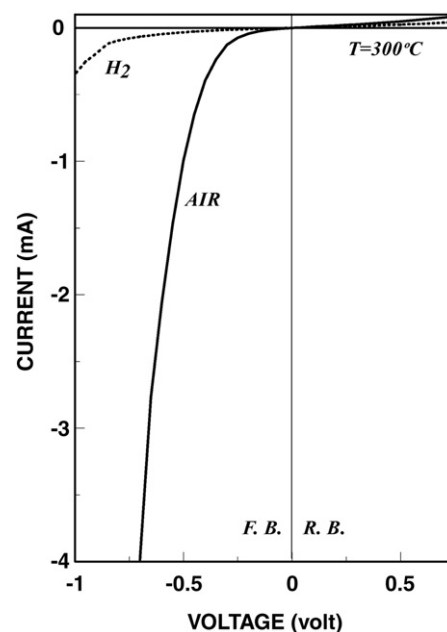


Fig. 15. *I-V* Characteristics of diamond-based H₂ sensor in air and H₂ environment at T=300 °C [163].

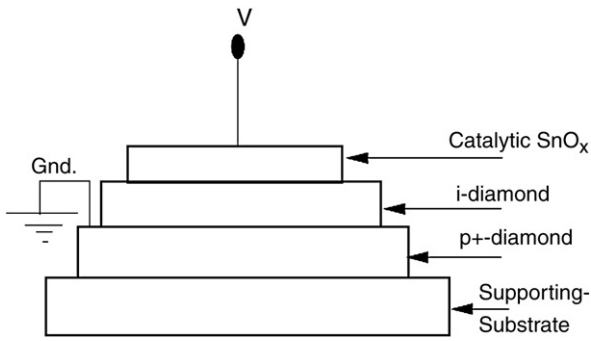


Fig. 16. A novel Pt/SnO_x/i-diamond/p+-diamond diode gas sensor [163].

SnO₂ film. Together with adsorptive oxide, undoped/insulative diamond forms the energy barrier for the carriers to allow current conduction. Therefore any electrochemical reaction, such as oxidizing or reduction process, taking place at the interface of catalytic-metal and insulative layers (SnO_x and insulative diamond) changes the energy barrier. This causes an exponential change in the CAIS diode structure. Chemisorption of oxygen by SnO_x at the surface and in the bulk changes the electrical properties of SnO_x, leading to the detection of oxygen gas. In addition, in the presence of reducing gases such as hydrogen and CO in the environment will lead to the reduction of pre-adsorbed oxygen in the device. This reduction reaction changes the electrical properties of SnO_x in opposite direction, enabling the detection of reducing gases. Finally, utilization of the catalyst, Pt, in conjunction with SnO_x lowers the operating temperature and enhances the sensitivity of the sensor by reducing the activation energy of the adsorption process. Fig. 17 shows the sensitivity to oxygen partial pressure at several temperatures. The negative slope indicates a decrease in device current upon oxygen adsorption. There is a rapid increase in ΔI at low oxygen concentrations, followed by a saturation trend at high oxygen concentrations. It was also observed that the oxygen sensitivity of the device increases with increasing temperature [163].

Gurbuz et al. [268] applied diamond chemical sensor to detect volatile organic compounds, such as benzene (C₆H₆) and toluene (C₇H₈) for possible indication of environmental hazard and petroleum in soil/subsoil environments. This diamond-based gas sensor consists of three important layers. They are the catalytic metal, intrinsic-diamond, and doped-diamond layers. Of which, the effect of i-diamond thickness plays a crucial role in determining the *I-V* characteristics of the sensor and its gas sensing behavior. For the purpose of demonstration, the authors fabricated two different i-

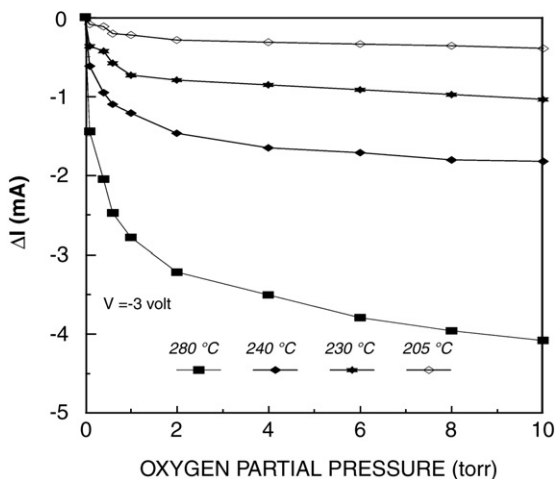


Fig. 17. Sensitivity to oxygen partial pressure at several temperatures [163].

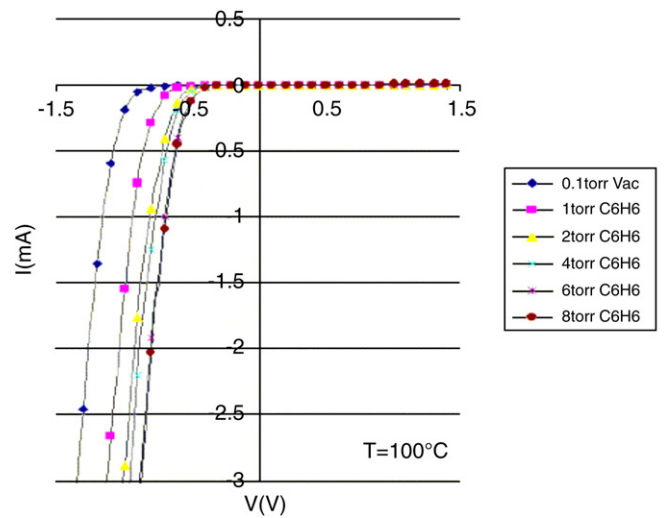
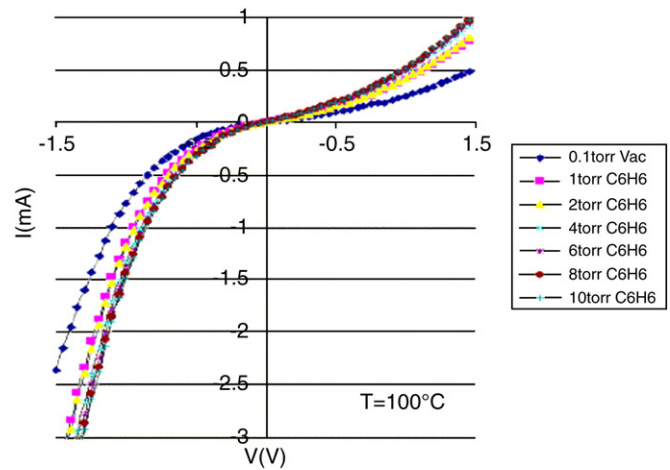


Fig. 18. *I-V* characteristics of the sensor with 0.17 μm of i-diamond (a) and 0.25 μm of i-diamond at 100 °C in different benzene concentration [268].

diamond thicknesses (0.17 and 0.25 μm) in the test sensors and characterized for benzene detection as shown in Fig. 18. Comparing the *I-V* characteristics shown in Fig. 18a and b, it is evident that the diode (rectifying) characteristics is significantly improved and the sensitivity to benzene is greatly enhanced. Fig. 19 shows a steady-state value of the current change (ΔI) versus benzene concentration at 100 °C with a fixed voltage bias. The curves show that the detection sensitivity, dynamic range and saturation limits are greatly improved with a thicker i-diamond layer (0.25 μm) in the sensor structure. From

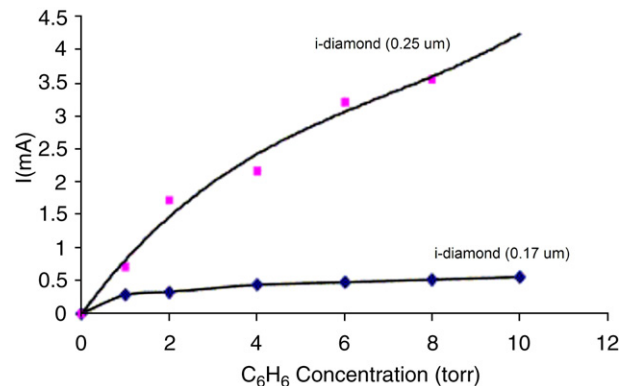


Fig. 19. Change in benzene sensitivity as a function of i-diamond thickness of the sensor [268].

the I - V characteristics, it is also evident that the diode rectifying behavior is significantly improved with $0.25\ \mu\text{m}$ of i -diamond thickness [268].

The same research group have studied toluene adsorption at the Pd/ i -diamond interface of the sensor by I - V characteristics (Fig. 20). Sensor was operated at 50 and 200 °C in different toluene concentrations. Fig. 20 shows a larger increase in the sensor current upon exposure to higher concentrations of toluene gas. A larger change in I - V characteristics at higher temperature for a constant toluene concentration was observed as shown in Fig. 20b. At a constant temperature, the change in device current reaches a maximum value at high toluene concentration. The exhibited higher current at a fixed voltage in benzene environments indicates that toluene is adsorbed as some forms of hydrocarbon radicals. The experimental results confirmed that Pd-gated diamond-based sensor is sensitive to toluene gas [268]. The use of diamond-film technology opens the door for the development of a microelectronic gas sensor that can operate at a wider and higher temperature range than the ones based on present silicon technology.

4. Potential applications of diamond-like carbon (DLC) for electrochemical sensors

Carbon-based materials play a major role in today's science and technology. Carbon is a very versatile element that can crystallize in

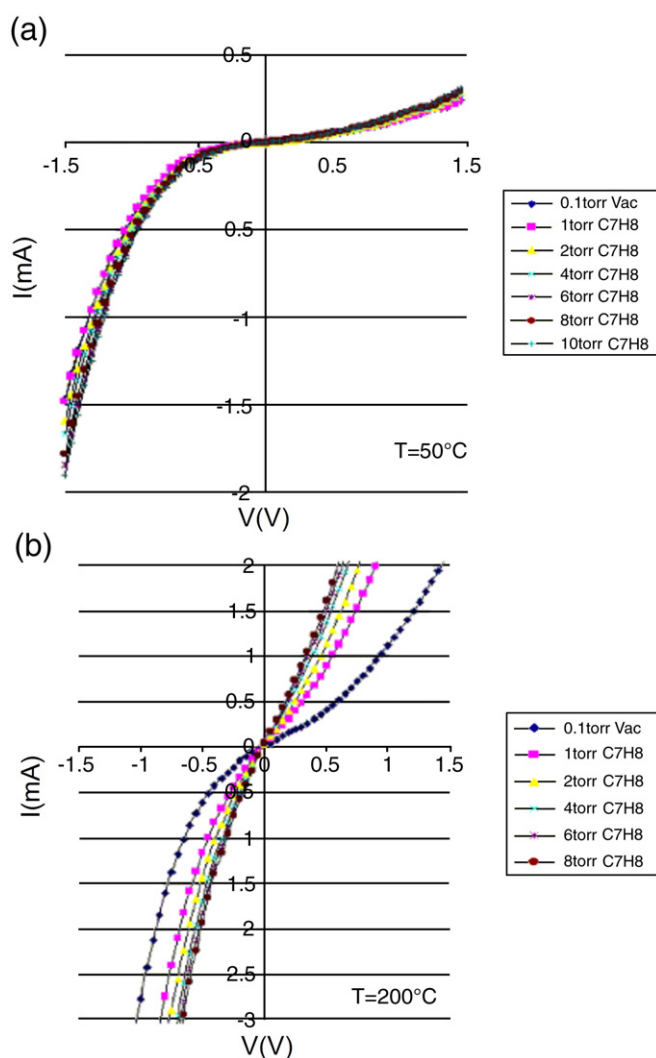


Fig. 20. I - V characteristics of the sensor at 50 and 200 °C in different toluene concentration [268].

the form of diamond and graphite. In recent years, there have been continuous and important advances in the science of carbon such as CVD of diamond [269] and the discovery of fullerenes [79], CNTs [55], and single-layer graphene [270]. There have also been major developments in the field of disordered carbons. In general, an amorphous carbon can have any mixture of sp^3 , sp^2 , and even sp^1 sites, with the possible presence of hydrogen and nitrogen. An amorphous carbon with a high fraction of diamond-like (sp^3) bonds is known as DLC. Unlike diamond, DLC can be deposited at room temperature, which is an important practical advantage. DLCs possess an unique set of properties, which can be changed by addition of other elements [54,55]. The DLCs and its modified forms have been applied for various engineering fields that has lead to a large number of applications, for example, magnetic hard disk coatings, wear-protective and anti-reflective coatings for tribological tools, engine parts, razor blades, sunglasses, biomedical coatings (such as hip implants or stents), and microelectromechanical systems [54,55,271–275].

Thin films based on DLCs are characterized to have excellent physical properties (high hardness, high elastic modulus) as well as chemical inertness to any acids, alkaline solutions or organic solvents [276]. By using such properties, thin layer of DLCs have also been applied to electrochemical measurements as electrode materials [276–278]. The high ohmic resistivity of DLC layers could be decreased by using doping, and the doped DLCs have been reported to have a wide electrochemical window range approximately from $-1\ \text{V}$ to $2.5\ \text{V}$ versus Ag/AgCl reference electrode. Such DLC layers are far more resistant to surface oxidation or reduction than conventional metal film, such as Au or Pt and no chemical interaction occur with metal deposits. Thus the long-term stability and reproducibility of the DLC layers for multiple electro-analyses are higher than the conventional metal film electrodes [279]. Additionally, microelectrodes pass so little current that they can be used in highly resistive electrolytes. When such microelectrodes are integrated as an array electrode, the magnitude of the sensor response is known to be increased more than two orders [280,281].

Recently, Kim [65] et al. reported a DLC microelectrode to commercial ELISA kits for medical diagnosis of viruses, such as HIV, HBV, and HCV. In this work, quantification of oxidized 3,3',5,5'-tetramethylbenzidine (TMB) was carried out by using a microelectrode made of boron-doped DLC and cyclic voltammetric analysis method without the conventional quenching step which uses sulfuric acid. The microelectrode provided well-known step-shaped graphs, and the detection limit could be improved by clear determination of electrochemical oxidative and reductive peaks. To demonstrate the applicability of DLC microelectrode to conventional ELISA kits, commercial ELISA kits for detection of HIV antigen, HBV antigen and HCV antigen were also tested. These results proved that the applicability of DLC microelectrode to practical detection is feasible.

Development of electrochemical glucose sensors have a practical significance, because such sensors can find important applications in many fields including biotechnology, clinical diagnostics and food industry. There are two main approaches to develop electrochemical glucose sensors. One is to use enzyme glucose oxidase which catalyzes the oxidation of D -glucose to form D -gluconolactone. A major drawback of enzymatic sensors is that they lack stability due to the intrinsic nature of enzyme. The other is the direct electrooxidation of glucose without enzyme [282–284]. The direct electrooxidation of glucose on different substrates such as platinum, gold alloys, copper, and different electrodes modified with copper, nickel, bismuth, silver, and mercury has been explored to develop effective enzyme-free sensors [285–289]. For most electrodes, only forward scan anodic current occurs during electrochemical process. However, both forward and reverse anodic currents occur at an electrode modified with Au nanoparticles and a boron doped diamond thin film electrode because of their strong catalytic effect [289,290].

Recently, Yang et al. [56] fabricated, Ni-doped DLC (NiDLC) thin films by magnetron co-sputtering deposition under different DC powers applied to a pure Ni target and a fixed DC power to a pure graphite target, at room temperature. The NiDLC thin films were used as working electrodes to electrocatalyze glucose oxidation in NaOH aqueous solutions with different glucose concentrations. It was found that direct electrochemical response of glucose at the NiDLC thin film electrodes gradually developed with increased glucose concentration in the electrolytic solutions. It was deduced that the Ni nanoparticles distributed on the NiDLC film electrode surfaces played a major role in promoting the glucose oxidation. Maalouf et al. [64] reported an amperometric glucose biosensor based on glucose oxidase immobilization on GC and DLC electrodes. The detection mode of this amperometric biosensor is based on the electrochemical detection of hydrogen peroxide, which is produced during the enzyme-catalyzed oxidation of substrates by dissolved oxygen. The detection limit of glucose on GOD/GC electrode was 20 μM while it was 50 μM on GOD/DLC electrode [64].

Wang et al. [291] has developed an amperometric sensor for the determination of acetic acid based on the DLC electrode. This sensor finds application in detection of acetic acid widely used in food, pharmaceutical and chemical industries. The DLC film was prepared by RF Magnetron sputtering deposition technique on a alumina substrate as shown in Fig. 21.

Fig. 22 shows the polarization curve of DLC electrode in 0.05 M trisodium citrate electrolyte in the presence of 1000 ppm acetic acid [291]. The sensing performance of acetic acid using DLC electrode have been explored. Different structures of the DLC films was examined by Raman spectroscopy as shown in Fig. 23. The results show that electrode sensitivity strongly depends on the sp^3 content of the DLC films. The optimized sensor reveals a linear response to acetate in the range of 12–300 ppm with relatively fast response time (5 s) [291].

Diamond and DLC thin films possess a number of unique and attractive properties that are not attainable from Si and other materials. These include high values of Young's modulus, hardness, tensile strength and high thermal conductivity, low thermal expansion coefficient combined with low coefficients of friction and good wear resistance. As a consequence, they are finding increasing applications in micro-electro-mechanical systems (MEMS). Applications of diamond and DLC films in MEMS are in two categories: surface coatings and structural materials. Thin diamond and DLC layers have been used as coatings mainly to improve the wear and friction of micro-components and to reduce stiction between microstructures and their substrates. The high values of elastic modulus of the diamond and DLC have been exploited in the design of high frequency resonators and comb-drives for communication and sensing applications. Chemically modified surfaces and structures of diamond and DLC films have both been utilized as sensor materials for sensing

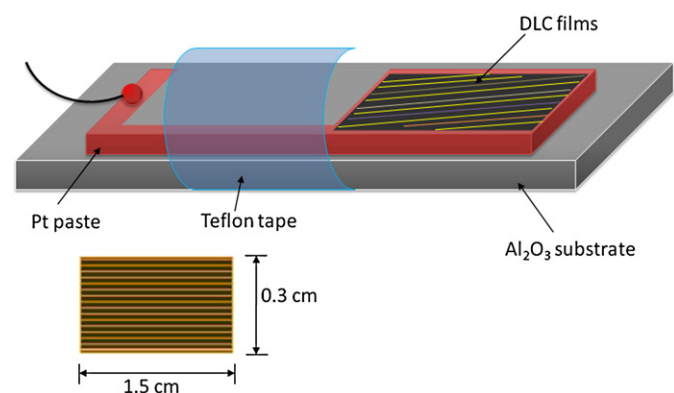


Fig. 21. Schematic drawing of DLC based working electrode [291].

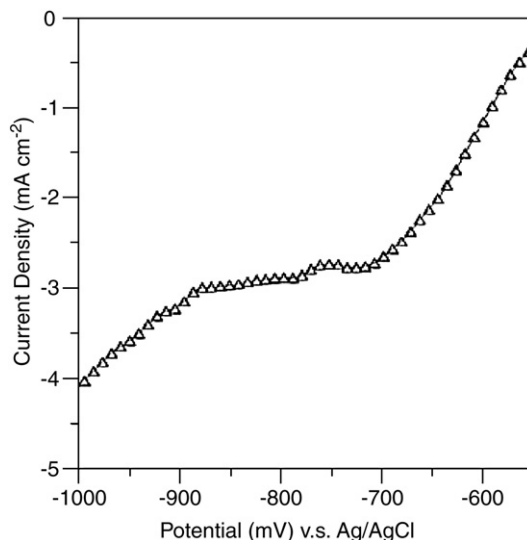


Fig. 22. Schematic drawing of DLC based working electrode [291].

traces of gases, to detect bio-molecules for biological research and disease diagnosis [292].

Some nanomedical applications demand a non-adhesive interface, while others may require complete tissue integration with the nanodevice. The latter requires biocompatible surfaces of engineered bioactivity, including nanostructured materials that promote and stabilize cell attachment. Atomically-precise diamond surfaces are readily available, so cell responses to these surfaces are yet to be seriously investigated. However, the biocompatibility of comparatively rough, bulk manufactured DLC surfaces has been addressed experimentally by a handful of researchers and diamond-coated orthopedic prostheses have been proposed, developed, or in clinical use [293–297]. For these experimental purposes, the apparatus coated with DLC is needed. Conductive surfaces of these sensor probes mostly need electrical insulating films coated on them, but it has been difficult to coat a high-quality and strong insulating film on a micro-acute probe such as a micropipette, especially on its tip. Thus the natural properties of DLC like non-adhesion and chemical inertness

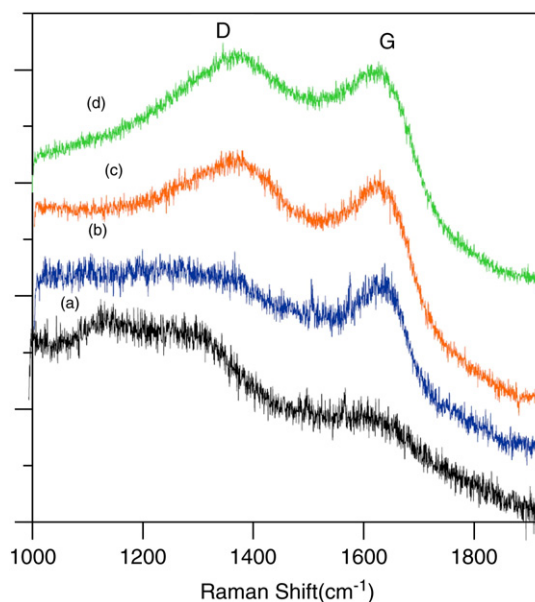


Fig. 23. Polarization curve of DLC electrode in 0.05 M trisodium citrate electrolyte containing 1000 ppm acetic acid [291].

can be employed to develop a wide range of sensors in biological fields.

5. Conclusion

As two important polymorphs of carbon, CNT and diamond have been employed as electrode materials for electrochemical sensing. The unique properties of CNTs, diamond and DLC films have contributed to a large extent for designing novel nanostructured electrochemical sensors and biosensors with improved analytical performance compared to conventional macro-structured electrochemical systems. The impressive role of these nanomaterials in modern electrochemical systems is supported by their advantages from an analytical point of view, such as the electrocatalytic ability of CNT-modified electrodes, NCD and doped DLC films. The enhanced active surface area and the anti-fouling capability of the modified surfaces are the added advantages of these materials that have led to a rising number of important electroanalytical applications over the years in various fields of interest.

CNT have become one of the most extensively studied nanostructures because of their unique properties. CNT can enhance the electrochemical reactivity of important biomolecules and can promote the electron-transfer reactions of proteins. The remarkable sensitivity of CNT conductivity with the surface adsorbates permits the use of CNT as highly sensitive nanoscale sensors. These properties make CNT extremely attractive for a wide range of electrochemical sensors ranging from amperometric enzyme electrodes to DNA hybridization biosensors. CNT sensor based fast diagnosis method using non-treated blood assay has been developed for specific detection of HBV.

Advances in the synthesis of highly conducting NCD thin films and nano wires have lead to an entirely new class of electrochemical biosensors and bio-inorganic interfaces. In addition, it also combines with development of new chemical approaches to covalently attach biomolecules on the diamond surface also contributed to the advancement of diamond-based biosensors. The feasibility of a capacitive field-effect EDIS platform for multi-parameter sensing is demonstrated with an O-terminated NCD film as transducer material for the detection of pH and penicillin concentration. This has also been extended for the label-free electrical monitoring of adsorption and binding of charged macromolecules. Diamond nano-wires can be a new approach towards next generation electrochemical gene sensor platforms. DLCs have also been applied to electrochemical measurements as electrode materials. DLC microelectrodes have been reported to commercial ELISA kits for detection of HIV antigen, HBV antigen and HCV antigen.

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