Electrochemical applications of carbon nanotube

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Abstract: Carbon nanotubes (CNT) have attracted the fancy of many scientists worldwide. The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications. In this review we describe the construction of the carbon nanotube paste electrode and discuss some of the electrochemical applications of nanotubes including: (i) batteries; (ii) electric double-layer capacitors; (iii) fuel cells; (iv) solar cells; (v) electrodeposition on its surface and (vi) electroanalytical sensing.

Keyword: N2 Carbon nanotubes; batteries; double-layer capacitor; fuel cell; solar cell; electrodeposition; electroanalytical sensors

1. Introduction

Carbon nanotubes have attracted particular interest due to their unique morphology, nanosized scale, novel physico-chemical properties and, furthermore, their versatile applications [1-6]. Carbon nanotubes could be visualized as rolled sheets of graphene (sp2 carbon arranged in a honeycomb lattice). There are two groups of carbon nanotubes, multi-wall carbon nanotubes (MWNTs) and single-wall carbon nanotubes (SWNTs) [7]. MWNTs can be visualized as concentric and closed graphite tubules with multiple layers of graphite sheet defining a hole typically from 2 to 25 nm separated by a distance of approximately 0.34 nm [7–9]. A SWNTs consist of a single graphite sheet rolled seamlessly, defining a cylinder of 1– 2 nm diameter. Carbon nanotubes can behave as metals or semiconductors depending on the structure, mainly on the diameter and helicity [7,9].

- **Electrical properties of carbon nanotubes**

Multi walled carbon nanotubes show superconductivity with a relatively high transition temperature [10]. Electron transport in nanotubes is described as ballistic, i.e. the resistance of the nanotube does not depend on its length as the mean free path λm is longer than the nanotube itself. $\lambda m = 30$ μm has been found by Berger et al. [6] which was much longer than the nanotube used. For SWNTs the theoretical limit of conductance is $GSWNT = 4e2/h$ where $e = 1.602 \times 10{-}19$. As is the electron fundamental charge and $h = 6.626 \times 10{-}34$ Nms, Planck's quantum [11]. Recent measurements of the magnetic properties of nanotubes indicate that SWNT might be the long sought material for room-temperature superconductors [12, 13].

- **Optical properties of carbon nanotubes**

One of the more recently researched properties of multi-walled carbon nanotubes (MWNTs) is their wave absorption characteristics, specifically microwave absorption. Numerous studies have been performed in the field of nanotube light absorption [14–16], Raman scattering [2,17], fluorescence [16,18] photoinduced molecular desorption [19] and nonlinear optical properties [20,21]. The photoconductivity of films of single-wall carbon nanotubes has been studied under continuous-wave near-infrared illumination. The photocurrent exhibits a linear response with the light intensity and with bias voltage up to 5 V. The temporal photoresponse of on/off step illumination shows a relatively slow relaxation time ∼ 4.3 s for films with a thickness of; 500 nm, which can be interpreted in terms of a kinetic model that takes into account the binding of photoelectrons with adsorbed oxygen. It was demonstrated that single-wall carbon nanotubes are capable of absorbing NIR light and generating a photocurrent under low applied bias [22].

2. Construction of carbon nanotube paste electrode (CNTPE)

Common types of carbon nanotube pastes are soft and non-compact, and have to be kept in special bodies. A holder for carbon pastes can be realized as a well drilled into a short Teflon rod, a glass tube, or a polyethylene syringe filled with a paste, which is electrically contacted via a conducting wire. Such constructions are very simple; however, there is one aspect which makes them not very convenient for practical use and this is the necessity of refilling the carbon paste in experiments requiring a regular removal of the electrode surface layer [23].

The electrode can be constructed by mixing graphite powder and multiwall carbon nanotubes in a mortar and pestle. Using a syringe, paraffin was added to the mixture and mixed well for 40 min until a uniformly-wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The percent of graphite, carbon nanotube and the mineral oil can be adjusted. A lot of searches used a ratio of 60:7:33 respectively and gave good results [24-26].

After the construction of the electrode, it should be electrochemically tested to investigate its electro-activity. Understanding the basic electrochemical properties of any new electrode such as CNTs is the key to making improved electrodes for a wide variety of applications. The standard solution of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple is used to investigate the electrochemical activity of CNTs electrode. Information about the types of diffusion that occur at electrode interfaces is of great importance; mass transport limitations need to be minimized and/or eliminated for applications such as catalysis, sensing and electrodeposition. In the case of catalysis in particular, enhanced diffusion leads to greatly increased reaction rates. It has been reported that the CNTs acted as an efficient electron transfer promoter. To illustrate the electron transfer kinetics, the voltammetry of two standard redox processes of $Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{3+}$ using MWCNTs. The rate of electron transfer was determined to be fast in that case [27].

3.   Applications of CNT in Electrochemical systems

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3.1. Batteries

3. 1.A. Lithium-ion battery

The outstanding mechanical properties and the high surface-to-volume ratio (due to their small diameter) make carbon nanotubes potentially useful as anode materials [28-33] or as additives [34] in lithium-ion battery systems. The electrode containing 10 wt % of carbon nanotubes as the additive displays a homogeneous distribution of nanotubes in synthetic graphite. With increasing weight percent of carbon nanotubes, the cyclic efficiency of the synthetic graphite battery anode increases continuously, and, in particular, when 10 wt % of the nanotubes was added, the cyclic efficiency was maintained at almost 100% up to 50 cycles. At higher concentrations, the nanotubes interconnect graphite powder particles together to form a continuous conductive network. The characteristics of a carbon nanotube when used as filler in the electrodes of lithium-ion batteries can be summarized as follows [35];

(i)   The small diameter of the nanotube makes it possible to distribute the nanotubes homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte.

(ii)   The improved electrical conductivity of the electrode is related to the high electrical conductivity of the tubes, and the function of the electrical bridge between graphite particles.

(iii)   The relatively high intercalation ability of nanotubes did not in itself lower the capacity of anode materials upon cycling.

(iv)   A high flexibility of the electrode is also achieved due to the network formation of the nanotube in a tube-mat structure.

(v)   The electrode has high endurance due to the presence of nanotubes, which absorb the stress caused by intercalation of lithium ions.

(vi)   Improved penetration of the electrolyte due to the homogeneous distribution of the tubes surrounding the anode material.

3. 1.B. lead-acid batteries

In order to increase the conductivity of electrodes in lead-acid batteries, different weight percents of carbon nanotubes are added to the active anode material (with average diameters of ca. 2–5 mm) of the positive electrode. The resistivity of the electrode is lowered for the case of 1.5% nanotube addition. When this sample (0.5–1 wt %) is incorporated in the negative electrode, the cycle characteristics are greatly improved compared with those of an electrode without additive [34]. This is probably due to the ability of carbon nanotubes to act as a physical binder, resulting in electrodes that undergo less mechanical disintegration and shedding of their active material. Therefore, it is expected that the use of carbon nanotubes as an electrode's filler should produce an enhanced cyclic behavior for electrodes in lead-acid batteries compared with electrodes using conventional graphite powder, because the unusual morphology of the carbon nanotube, such as the concentric orientation of their graphite crystallites along the fiber cross-section, induces a high resistance towards oxidation, and furthermore the nanotube network embedded in the polymer would enhance the reactivity of the electrode [35].

3.2. The electric double-layer capacitor

The merit of the electric double-layer capacitor (EDLC) is considered to be a high discharge rate [36], which makes them applicable as a hybrid energy source for electric vehicles and portable electric devices [37]. EDLCs containing carbon nanotubes in the electrode exhibit relatively high capacitances resulting from the high surface area accessible to the electrolyte [33,38,39]. On the other hand, the most important factor in commercial EDLCs is considered to be the overall resistance. In this context, carbon nanotubes with strong electrical and mechanical properties can be used as an electrical conductive additive in the electrode of EDLC. It has been demonstrated that the addition of carbon nanotubes results in an enhanced capacity at higher current densities, when compared with electrodes containing carbon black [40]. It has been reported that supercapacitor electrodes, prepared from catalytically grown multi-walled CNTs whose surface area is 430 m2/g, show a maximum specific capacitance of 113 F/g and a power density of a 8 kW/kg at an energy density of 0.56 Wh/kg in a solution of 38 wt% H2SO4 used as the electrolyte [38]. Carbon nanotubes uniformly 50 nm in diameter were directly grown on graphite foil. Cyclic voltammetry (CV) shows that the carbon nanotube/ graphite foil electrode has a high specific capacitance (115.7 F/g

at a scan rate of 100 mV/ s) and exhibits typical double-layer behavior. A rectangular-shaped CV curve persists even at a scan rate of 100 mV/ s in 1.0 M H2SO4 aqueous solution, which suggests that the carbon nanotube electrode could be an excellent candidate as the electrode in electrochemical double-layer capacitors. In addition, the influence of the potential scan rate, aging, and the electrolyte solution on the specific capacitance of nanotube electrodes was also studied. These results show that the carbon nanotube electrode could be an excellent candidate in electrochemical double-layer capacitors [41]. The effect of electrochemical oxidation in 0.2 M HNO3 for multi-walled carbon nanotubes (MWNTs) on the performance of electrochemical double layer capacitors (EDLCs) was studied. Scanning electron microscope and transmission electron microscope images reveal that electrochemical oxidation increases the specific area of MWNTs by cutting off the nanotube tips. Cyclic voltammetry and constant current charging/discharging was used to characterize the behavior of EDLCs of the oxidized-MWNTs in 1.0 M H2SO4. The specific capacitance of the oxidized-MWNTs was remarkably improved [42].

3.3. Fuel cell

Fuel cells have been considered as next-generation energy devices because these types of systems transform the chemical reaction energy from hydrogen and oxygen into electric energy. Carbon nanotubes decorated with metal nanoparticles as electrodes have doubled the fuel performance due to increased catalytic activity of nanotube-based electrodes [43]. It has been reported the efficient impregnation of Pt nanoparticles (OD < 3 nm) on the carbon nanotubes. The high power of PtRu/CSCNT electrodes proposes practical interest and importance for applications for various devices [44]. The use of multiwalled carbon nanotubes as a platinum support for proton exchange membrane fuel cells has been investigated as a way to reduce the cost of fuel cells through an increased utilization of platinum. Carbon nanotubes were employed as the support for the subsequent platinum catalyst, which is electrodeposited on the carbon nanotubes. The feasibility of a fuel cell using the carbon nanotube-based electrodes was improved [45]. It has been found that the Pt/CNTs electrode can be used to construct a methanol sensor to be used with DMFC fuel cells. The fabricated Pt/CNTs electrode shows superior performance vis-a Pt wire electrode for methanol oxidation in CV measurement. The combined results indicate that Pt electro-deposited CNTs (Pt/CNTs) electrode can be a promising candidate for methanol sensor for fuel cells application [46]. Using CNTs as supports for cathode catalysts in a direct methanol single cell produces better performance compared to XC-72 carbon. The high electro- catalytic activity may be attributed to the unique structure and better electric properties of the CNTs, as well as to the specific interaction between Pt and CNTs [47]. A high Pt loading of 32.5% on CNTs are used as electrocatalyst for the oxygen reduction reaction in polymer electrolyte membrane fuel cells (PEMFCs). For high performance in fuel-cells, CNTs have to be functionalized to have a uniform dispersion with a narrow Pt particle range, rather than a higher loading of platinum [48].

3.4. Solar cells

Carbon nanotubes (CNTs) have attracted great attention in improving photovoltaic performance of dye-sensitized solar cells DSSCs because of their high electrical conductivity, chemical stability, high surface area, and tubular structure [49–57]. High electron affinity at CNTs can be used to act as electron collector and to enhance carrier mobility in DSSCs.

The performance of dye-sensitized solar cells (DSSCs) by applying carbon nanotubes (CNTs) to the counter electrode using two different methods: screen printing and chemical vapor deposition was investigated. When the highly purified and aligned CNTs were used as the counter electrode, a conversion efficiency of DSSCs of over 10% was recorded. This CNT-deposited counter electrode shows higher photoconversion efficiency than CNT-printed and Pt-coated electrodes under the same conditions. The large surface area and high electron conductivity of CNTs contributed to the high DSSC cell efficiency. The CNT-based counter electrodes could herald a new route to producing non-platinum-based counter electrodes in DSSCs devices [58,59]. Studies were performed on Dye-sensitized solar cells (DSSCs) using multiwalled carbon nanotube (MWCNT)–TiO_2 nanocomposite as a light scattering layer. Internal resistance in the DSSC was characterized by electrochemical impedance spectroscopy (EIS). EIS results reveal a decrease in the charge resistance of electrolyte/dye/MWCNT–TiO_2/TiO_2 interface with increasing MWCNT content up to 3 wt% which leads to an improvement in the photovoltaic performance. Compare with a nanocrystalline TiO_2 single-layer cell, the DSSC based on the MWCNT (3 wt%)–TiO_2/TiO_2 bilayer structure photoelectrode shows ~100% increase in solar-to-electric energy conversion efficiency, which is attributed to the inclusion of MWCNTs in TiO_2 matrix. the photovoltaic conversion efficiency should be obtained with both MWCNT [60].

3.5. Electrodeposition of metal nanoparticles on carbon nanotubes

Electrodeposition offers many advantages over high temperature metal deposition for metal nanoparticle formation on SWNTs. One of the most significant advantages of electrochemical deposition is the ability to control size and distribution of nanoparticles by varying potential, time or solution concentration. Most studies involving metal nanoparticle electrodeposition focus on noble metals such as Ag, Au, Pt, and Pd [61–67], with a few exceptions Ni, Cu [68- 70], primarily due to the need for components of alternate energy sources. Electrodeposition of metal nanoparticles on carbon nanotubes depends on various parameters, such as pretreatments, method of manufacturing for SWNTs, type of SWNTs, distance of the nanotubes from contact electrode, density of SWNTs in network, etc. As mentioned in the previous section, oxygen functionalities serve as axial ligands for metal nanoparticle precursors to bind to the SWNTs. Therefore, the most common pretreatment methods involve treating them with strong acids or oxidizing agents such as H_2SO_4/HNO_3, H_2SO_4/H_2O_2, HNO_3, O_3, and $KMnO_4$. This is essentially a controlled method of damaging the tubes [68,71,72].

An alternative pretreatment method, involving a more gentler electrochemical oxidation, was studied [62,73]. Oxide functional groups at defect sites on the ends and sidewalls of SWNTs were produced by cycling electrochemical potential in 0.5M sodium sulfate, following a similar procedure used for activating glassy carbon electrodes [74]. They employed a three-step process to deposit Pd and Pt nanoparticles on the SWNTs: (1)

pretreatment by potential cycling, (2) formation of octahedral complexes of Pt(IV) or Pd(IV) and (3) conversion of surface complexes to metal atoms by additional potential cycling. The density of Pt nanoparticles was higher on the thicker bundles than on thinner bundles because of the presence of a higher number of carboxylic acid groups on thicker bundles. The electrodeposition of Au, Pt and Pd on SWNT nanoelectrode arrays deposited on non-conductive supports has been studied [64]. The average nanoparticle size could be controlled by varying the applied potential and metal salt concentration. Uniform sized nanoparticles were obtained at sufficiently negative potentials. Day et al. have investigated the electrodeposition of Ag and Pt on high-density SWNT networks [75], forming either dispersed nanoparticles, or continuous metal nanowires on these networks, depending on the distance from contact electrode. The driving potential for electrodeposition decreased with increased distance from the metal contact electrode. Therefore, the rate of nanoparticle nucleation and growth increased at close proximity to the contact electrode, resulting in continuous nanowires, rather than separate nanoparticles, near the contact electrode. Day et al. have also investigated the parameters controlling nanoparticle density, size and distribution for the case of Pd and Pt deposition on SWNT networks [65]. Pd and Pt were deposited at various potentials and it was determined that deposition potential and time are important factors in determining nanoparticle size and density. One interesting observation they made was that when Pd deposition was done at very low deposition overpotentials, nucleation took place preferentially at defect sites on SWNTs. However, when higher deposition overpotentials were applied, nanoparticle deposition at pristine regions of the SWNTs was also initiated. Chen et al. proposed changing the size of Pt nanoparticles by changing the viscosity of the electrolyte and adjusting the number of potential pulses used during deposition [76]. Aqueous solutions of H_2PtCl_6 were used as electrolyte and the viscosity of the solution was varied by adding different quantities of glycerol. Tuning the viscosity was proposed as a means to control the growth of Pt nanoclusters due to controlling the diffusion of Pt(IV) ions. The shape of a nanoparticle is significant because catalytic and sensing properties depend on the arrangement of surface atoms. Studies to control the shape of the Pd nanoparticles electrodeposited on SWNTs have indicated that smooth and flat facets of Pd nanocubes were electrodeposited on SWNTs on porous anodic alumina templates at sufficiently lower current densities 1.0 $mAcm^{-2}$ [77]. Arai et al. have reported electrodeposition of Cu and Ni on carbon nanotubes [69,70]. For the case of Ni deposition, they demonstrated selective deposition of Ni on the ends and defect sites of MWNTs. This has been attributed to the high electrical conductivity of MWNTs in the axial direction and easy electron transfer in defect sites. Ni-coated SWNT nanowires were also made by electrodeposition on SWNTs supported on alumina membranes [78]. Electroplating of Au on semiconducting SWNTs was found to reduce the contact resistance between semiconducting SWNTs and Pd electrodes on which the nanotubes were fabricated [79]. Electrodeposition of platinum nanoparticles (Pt NPs) on CNTs is usually carried out at -0.25 V in an electroplating bath containing H_2PtCl_6 and H_2SO_4 under gentle stirring [80]. CNTs with PtNPs are obtained by reducing $H_2Pt(NO_2)_2SO_4$ with $NaBH_4$ in the dark with constant stirring [81]. Alternatively, CNT based electrodes can be immersed in a solution of K_2PtCl_4 and K_2SO_4. The electrooxidation of $PtCl_4^{2-}$ is conducted on CNTs at 0.3 to 1.3 V until no distinct anodic peaks are observable. The CNT electrode is removed and electroreduced at -0.25 V in 0.1 M H_2SO_4 for 2 min, resulting in the deposition of Pt NPs on CNTs [82]. Gold nanoparticles (Au NPs) are electrochemically deposited onto CNTs from a solution of $HAuCl_4$ by cycling the potential between 1.0 and 0.0 V vs. saturated calomel

electrode [83]. Copper nanoclusters are electrochemically deposited on CNT electrodes by applying a potential of −1.0 V in a degassed Na2SO4 and CuSO4 solution. Cu nanoparticles (CuNPs) can also be prepared by reducing copper dodecyl sulfate using sodium borohydride, followed by binding with SWCNTs [84]. The electrodeposition of silver and gold usually requires stabilizers in order to obtain regular particles [85,86]. Silver nanoparticle deposition onto SWCNTs has also been reported in the absence of a stabilizer [87]. The size and distribution of the nanoparticles can in general be controlled by the magnitude of the applied potential and the concentration of the metal salt in solution. However, the growth kinetics can vary substantially from one metal to another [88]. For example, Ag nucleates much faster than Pt on the bare nanotube and thus by varying the time of deposition the density of Ag nanoparticles can be controlled, while with Pt nanoparticles increasing the deposition time results in bigger clusters. In another study, nickel has been electrodeposited in a controlled manner onto individual SWCNTs. After oxidative dissolution and re-deposition of Ni, the particles were found at exactly the same positions as before [87].

3.6. Carbon nanotube as a sensor for electroanalytical applications

An important part of the impressive success of the use of CNTs for electroanalytical applications is probably due to the ability of this nanomaterial to promote electron transfer in electrochemical reactions. The electrocatalytic effect of CNTs has been attributed to the activity of edge-plane-like graphite sites at the CNT ends [88]. Carbon nanotubes have been applied for the detection of analytes at lower potentials than at some other electrode materials. Analytes which have been monitored at nanotube modified electrodes include dopamine [89,90], ascorbic acid [90,91], uric acid [91,92], norepinephrine [93], NADH [94-96] and hydrogen peroxide [91,97]. These analytes are all molecules, which are important in a biological context with hydrogen peroxide and NADH being particularly important for the interfacing nanotube modified electrodes with enzymatic detection of analytes as in enzyme biosensors. The monitoring of an enzyme reaction by detecting the hydrogen peroxide produced was illustrated by Wang et al. [97]. The nanotube modified glassy carbon electrode showed the onset of the oxidation of hydrogen peroxide at +0.2V versus Ag/AgCl whereas on a bare glassy carbon electrode no H2O2 oxidation was observed up to +1.0V. The low potential for H2O2 oxidation was consistent with the observation of Rubianes and Rivas at a nanotube-paste electrode [35] where hydrogen peroxide oxidation was reported at +0.3V versus Ag/AgCl. Hydrogen peroxide is detected at platinum electrodes at around 650 mV (some 300 mV more cathodic) [98].Wang et al. [97] incorporated the nanotube modified electrode into a flow injection apparatus to detect glucose by monitoring the H2O2 produces in the enzyme reaction between glucose oxidase in the carrier solution and glucose. Significant glucose response could be observed at −0.05 V with negligible interference from common interferences acetamidophen, ascorbic acid and uric acid. The voltammetric study of quercetin has been carried out at a multi-walled carbon nanotubes-paraffin oil paste electrode (CNTPE). Quercetin exhibits a very sensitive and well-defined anodic peak at it, and the signal to blank current ratio is higher in comparison with corresponding graphite paste electrodes and CNTs casting film modified glassy carbon electrodes [99].

Because of the strong sorption properties of CNTs, their application on the surface of working electrode has allowed several original methods of stripping voltammetry to be developed. In stripping measurements of several organic

analytes, the first step of determination (sorption of analytes) has been carried out at open circuit on electrodes modified with CNTs. In the next step, the electrochemical oxidation or reduction of accumulated analyte is carried out. These procedures have been developed for anodic determination of xanthine [100], 6-benzylpurine [101] and fluphenazine [102], as well as for determination of 4-nitrophenol based on a very sensitive, well-defined reduction peak at the SWCNT-modified GCE [103]. In the first stage of voltammetric stripping determination of transition metal cations with electrodes modified with MWCNTs, cations have been adsorbed from solution containing iodide, then reduced at -0.6 V (Hg2+ [104]) or -1.2 V (Cd2+ and Pb2+ [105]), and, in the last step, anodic stripping has been employed. Such methods are alternatives to conventional anodic stripping voltammetry using thin-film mercury electrodes. Stripping voltammetry of Cd(II) was reported using a GCE modified with an MWCNT/Nafion composite film [106]. Conventional anodic stripping voltammetry of Cd(II) with a GC disk electrode has been used to detect DNA hybridization based on CNTs loaded with CdS tags [107]. The sandwich hybridization assay combined the use of CNTs carrying a large number of CdS-particle traces, capped earlier with octadecanethiol, with sensitive detection of CdS-nanoparticle traces. The analytical applications of CNTs in developing electrochemical biosensors have already been partly reviewed [108,109]. Most favorable is direct attachment (e.g., of proteins) to CNTs, already mentioned in immobilizing cytochrome c [110] and hemoglobin [111]. In both these cases, the direct transfer of electrons between electrodes and proteins was observed. Non-covalent functionalization of CNTs has been reported for binding of specific proteins and detection of clinically important biomolecules such as antibodies associated with human autoimmune diseases [112]. Among the various reported designs of CNT-based enzymatic biosensors, the simplest are those where enzyme was entrapped in the MWCNT paste, as described for glucose oxidase [91], or where enzyme was physically adsorbed on the electrode surface modified with MWCNT, as reported for a screen-printed biosensor with organophosphorus hydrolase [113].

There have been a number of examples of immobilizing biomolecules onto carbon nanotube modified electrodes for the purpose of fabricating electrochemical biosensors. One such example is the immunosensor of Wohlstadter et al. [114] for the detection of α-fetoprotein (AFP). The immunoassay was a sandwich assay where antibodies were immobilized on the MWNT/EVA composite electrode. Capture of AFP resulted in binding of a Ru(bpy)33+ labeled antibody. As the Ru(bpy)33+ is chemiluminescent, binding is transduced by the release of light upon poising the electrode at potentials more anodic than +1V. The immunosensor had a detection limit of 0.1nM with a linear range up to 30 nM. Ru(bpy)33+ was also used in the transduction of DNA hybridization in the DNA biosensor developed by Meyyappan and co-workers [115-118]. Amine terminated probe DNA was immobilized onto the ends of aligned MWNT arrays using carbodiimide chemistry. The probe DNA had inosine bases substituted for the normally occurring guanine bases, which are the most easily oxidized bases. The target sequence was labeled with 10 guanine bases at one end. Hybridization in the presence of Ru(bpy)33+ allowed highly sensitive detection of DNA. The Ru(bpy)33+ oxidizes the guanine bases on the target sequence and is reduced to Ru(bpy)32+. The Ru(bpy)32+ then diffuses to the electrode where it is oxidized back to Ru(bpy)33+, thus forming a catalytic cycle as first described by Thorp and co-workers [119,120]. The DNA biosensor was estimated to have a detection limit as low as 6 a mol, which is exceedingly low compared with other DNA electrochemical biosensors [121]. The advantage in using the

nanotube modified electrode in this case was the low signalto- noise ratio found with nanotube electrode arrays which enabled such a the low detection limit to be achieved.

Carbon nanotube modified electrodes have also been used of the immobilisation of enzymes and other redox proteins on the ends of aligned nanotube arrays [122,123], on the walls of carbon nanotubes [124-126] and inside nanotubes [127]. The vast majority of these studies into the immobilisation of enzymes are for the development of electrochemical enzyme biosensors. A study by Azamian et al. [124] demonstrates the principle where glucose oxidase is adsorbed along the length of carbon nanotubes randomly distributed on a glassy carbon electrode. In the presence of glucose and ferrocene as a mediator, the glucose signal was 10-fold greater than if glucose oxidase was adsorbed onto the glassy carbon electrode alone. In this case, the advantage conferred by the nanotubes is to provide a high surface area electrode to which the glucose oxidase can adsorb. Hence, the greater signal arises from the greater amount of active enzyme at the electrode interface [128].

Conclusions

A widespread number of publications that directly or indirectly show the relation of CNTs with electrochemistry or at any rate aspires of future interest in this science are revised. The unique electrical, mechanical, and chemical properties of CNTs have made them intensively studied materials in the field of electrochemistry between other fields.

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