1. Buckypapers for bioelectrochemical applications

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Chapter 1: Buckypapers for bioelectrochemical applications

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1.1 Introduction to buckypapers for bioelectrochemistry

Buckypapers are self-supporting nanostructured thin films of entangled carbon nanotubes (CNTs), resembling an electronic paper, which are held together by pi-pi stacking and interweaving interactions. Richard Smalley's group first reported the formation of carbon nanotube sheets in 1998 (coining the term "bucky paper") as a method for characterizing the production quality of CNTs.[1] Carbon nanotube buckypapers and their composites have excellent prospects for a wide range of applications from aerospace materials[2] to sensors[3,4] and fuel cells[5,6], and are thus of interest to a vast research and industrial community. Over the last 5-7 years, buckypaper materials have emerged for the construction of implantable, wearable and portable bioelectronic devices owing to their properties including high conductivity and porosity, flexibility, lightweight, biocompatibility, and the ability for electron transfer with enzymes and microbes[7]. In addition to being used for enzymatic and microbial biofuel cell construction[7–9], buckypapers are also emerging for hybrid supercapacitors[10], photoelectric biofuel cells[11], and other bioelectronic systems including biosensors[4,12], bioreactors[13] and biologic devices[14].

Buckypaper is the accepted term for carbon nanotube sheets, disordered or aligned, formed by vacuum filtration of aqueous (*e.g.* in the presence of a non-ionic surfactant such as Triton X-100) and non-aqueous dispersions (*e.g.* in *N*,*N*-dimethylformamide, DMF) of single-walled, double-walled and multi-walled carbon nanotubes (SWCNTs, DWCNTs, and MWCNTs)[1,6,15]. Sonication, centrifugation and additional filtration steps are also commonly used to improve the quality and purity of the CNT dispersion prior to filtration through a porous membrane[6,15]. Free-standing "lab-made" buckypaper sheets are finally obtained after washing, drying, and peeling from the underlying membrane. "Commercial" buckypaper prepared by continuous manufacturing is a popular type of buckypaper. The MWCNT buckypaper from Buckeye Composites (a division of NanoTechLabs, USA) is the most widely reported commercialized buckypaper for bioelectrochemical applications[16–19]. In addition to vacuum filtration, lab-made buckypaper can also be prepared via methods including domino-pushing[20], CNT winding[21] and by using a lab-scale hand sheet former[22]. The most common type of buckypapers used in bioelectrochemistry are illustrated in Figure 1.1.

Buckypaper fabrication is conceptually straightforward but factors such as dispersion homogeneity, CNT type and chemical functionality, membrane porosity, and the presence of

additives in the dispersion, all create differences with respect to material reproducibility and functionality. Several studies have focused on tuning the physical and mechanical properties of buckypaper such as porosity, Young's modulus, hardness and electrical conductivity[15,22–30]. For example, Shen *et al.* investigated CNT length and showed how this parameter strongly governed the viscoelasticity and permeability of buckypaper[30]. Whitby *et al.* demonstrated that the porosity of buckypaper could be tuned using different casting solvents[29]. Oh *et al.* revealed the crucial roles of CNT suspension concentration and filtration velocity for self-assembled alignment of buckypaper to enhance the mechanical properties[15]. In our recent electrochemical study, we compared the physical, chemical, electrochemical and bioelectrocatalytic properties of lab-made and commercial buckypapers[16].

For bioelectrochemical applications, surfactant-free methods of producing buckypaper are highly desirable owing to the undesirable impact of residual surfactant on conductivity and biocompatibility risks such as cell lysis[6,16,29]. Buckypaper prepared from non-aqueous solvents such as DMF or alcohols without surfactant has been reported with success, for example, owing to improved CNT-solvent and the possibility to dissolve a wide range of chemical modifiers[6,22,31–33]. However, the removal of non-aqueous solvents is crucial to minimize enzyme denaturation, microbe deactivation and material toxicity, in particular for in-vivo applications.

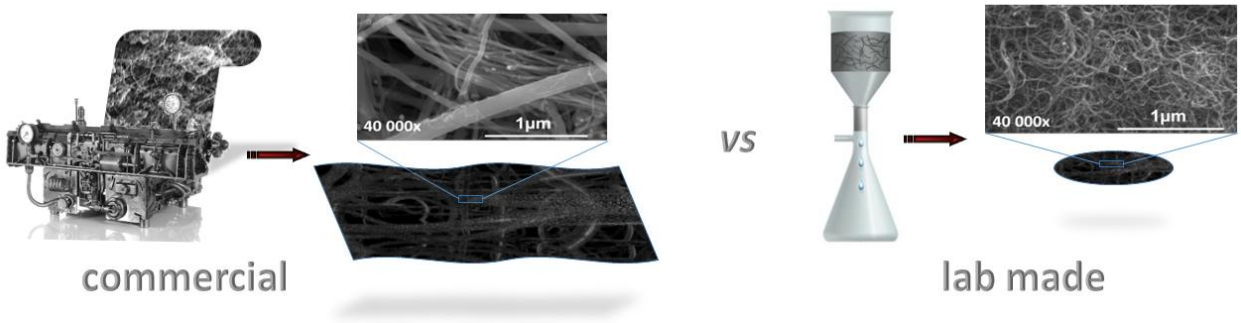

Figure 1.1: Illustration of fabrication procedures for commercial and lab-made buckypaper via mass production and lab-scale vacuum filtration, respectively.

Porous 3D-nanostructured carbon structures based on CNTs[34], mesoporous carbons[35,36] and carbon black[37] have become privileged conducting supports in bioelectrode design. Many of the best performing enzymatic bioelectrodes to date have been fabricated using CNTs due to their high specific surface area and exceptional electronic and mechanical properties, for example, that allow effective direct and mediated electron transfer with enzymes for bioelectrocatalysis[8,34]. Porous 3D-nanostructured carbon electrodes are particularly attractive due to the high surface/volume ratio

which increases the loading of catalyst per geometric area. The size and curvature of pore and nanotube structures (e.g. nano-, micro- and meso-pores), and their surface chemistry, play a crucial role on the bioelectrocatalytic parameters of the electrode, such as mass transport, enzyme orientation and activity, and electron transfer kinetics[16,35,38,39].

An important aspect which is frequently overlooked in bioelectrode design is the development of porous electrodes with practical physical properties for their target application. For example, for wearable biofuel cell and biosensor applications, "skin-like" electrodes which are soft, bendable, and even stretchable are required[40,41]. For implantation, compact and lightweight electrodes are required with flexible geometries and superior stability and biocompatibility[7,42]. Many bioelectrodes, including 3D-nanostructured electrodes, are prepared via the simple adsorption of nanocarbons (MgO-templated carbon[35], mesoporous nanoparticles[43], and Ketjen black[37], for example) onto robust but bulky and non-flexible glassy carbon supports. The resulting thin films can also be fragile and prone to delamination from the electrode. Bulk CNT "pellet" electrodes formed by compression in the presence of enzyme emerged as a more practical solution to glassy-carbon-based electrodes implantable biofuel cells; however, the pellet electrodes were still quite cumbersome, fragile and brittle[44,45]. For wearable applications, carbon electrodes based on printed CNT inks and pellets supported on a flexible substrate have been developed[46,47].

Buckypaper is an alternative form of 3D-nanostructured electrode which is the electrode itself (no support is required) and has attractive qualities for interfacing biological and electrochemical systems for bioelectrochemical applications[7]. Compared to the existing CNT pellet bioelectrodes, for example, buckypapers offer a higher density of CNTs per surface area and improved stability owing to their more compact structure. A comparison of the quantity of enzymes used per electrode also reveals that buckypapers are more economical than CNT pellet electrodes[6,48]. Nevertheless, buckypapers do suffer from being brittle and fragile in several cases. In addition, lab-made fabrication of buckypapers can also require the use of significant amounts of organic solvent.

1.2 Biological fuel cell devices

One of the important applications of buckypaper is in the field of biofuel cells[7]. Buckypaper electrodes have been used in implanted bioelectronic devices since 2012. Notably, enzymatic biofuel cells based on commercial buckypaper have been implanted in different animals and used for in-vivo energy harvesting and device powering via the organism[17,49]. Biofuel cells are emerging power sources which can generate clean electrical energy from chemical substrates present in various media such as biofluids and environmental waters using enzymes (enzymatic biofuel cells) or

microorganisms (microbial biofuel cells) as the catalysts[8]. Power is generated from bioelectrochemical reactions via the oxidation of fuels such as hydrogen and sugars (at the anode), and the reduction of oxidants such as oxygen (at the cathode). Biological fuel cells offer advantages compared to conventional batteries and fuel cells including the use of renewable and non-toxic catalysts and fuels. Enzymatic biofuel cells are considered as promising power sources for low-power electronic devices for short periods (e.g. 3 months to 1 year) whereas microbial biofuel cells are better suited for large-scale powering and industrial applications over longer periods (e.g. years). A short discussion highlighting some of the latest innovations in biofuel cell research, as well as some of the hype, can be found in our recent opinion article[50].

1.2.1 Implantable enzymatic biofuel cells

Katz and coworkers were the first to report the use of buckypaper for the construction of enzymatic biofuel cells. In their pioneering research, the buckypaper-based biofuel cells were implanted in snails,[17] clams[51], rats[52] and lobsters[49] and operated for durations ranging from a few hours to several weeks. The open circuit voltages (OCVs) and maximum power outputs of the biofuel cell devices ranged from 0.14 V to 0.54 V (up to 1.2 V for anode-cathode pairs connected in series)[49] and *ca.* 0.5 μW to 160 μW, respectively. The implanted biofuel cells exploited commercial MWCNT buckypaper (Buckeye Composites) modified with adsorbed pyrroloquinolinequinone-dependent glucose dehydrogenase (PQQ-GDH) at the anode, for glucose oxidation, and laccase from *Trametes versicolor* (*Tv*Lc) at the cathode, for oxygen reduction. The glucose/O_2 biofuel implanted in the shell of the snail which operates from the hemolymph is depicted in Figure 1.2. Buckypaper proved to be an effective choice due to its bioelectrocatalytic performance as well as its physical properties such as sub-mm (typically 5-200 μm) thickness, flexibility, and shapeability, which facilitated their insertion via small incisions into the organisms (e.g. in lobsters)[49] or their conformal contact with internal muscle tissues (e.g. in rats)[52].

In an early fascinating experiment, Katz and coworkers demonstrated that feeding the snail, or allowing it to rest for up to 1 hour, allowed the power output of the biofuel cell to be restored via substrate diffusion and metabolism[17]. The stable operation of the implanted biofuel cell over two weeks highlighted practical stability and limited inhibition and fuel cell deactivation. Katz and coworkers later demonstrated the connection of implanted biofuel cells in series and the possibility to produce sufficient energy to turn an electric motor or an electronic watch[49,51]. In another breakthrough, the connection of five buckypaper biofuel cells in series generated an OCV of 2.8 V in

human serum, highlighting the potential of buckypaper biofuel cells to meet the *ca.* 1.4 V requirement to power a range of low-power microelectronic devices without a voltage boost convertor[49].

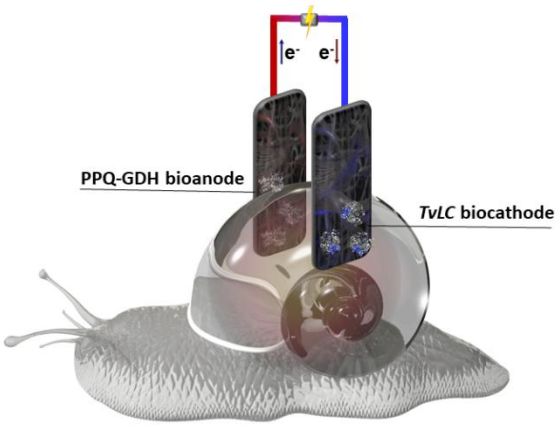

Figure 1.2: Cartoon of an implanted glucose/oxygen biofuel cell inserted via incision of two buckypaper bioelectrodes in the snail's shell.

1.2.2 Wearable enzymatic biofuel cells

Enzymatic buckypaper electrodes have great potential in the emerging field of wearable biofuel cells owing to their attractive properties, depending on the fabrication methods used, such as their flexibility and skin-conformability under bending[7,53]. Compared to implantable biofuel cells that require surgical procedures, wearable biofuel cells can be mounted on (i.e. non-invasive) or inserted in (i.e. minimally-invasive) the body without the need for surgical intervention. Wearable devices are therefore somewhat easier to develop and more user friendly compared to implantable devices. Skin-based wearable biofuel cells which exploit human sweat are popular as sweat is easily accessible, can be produced in high quantities, and contains attractive fuels such as lactate and glucose. Lactate is particularly attractive owing to its high concentrations of *ca.* 10 to 100 mmol L^{-1} compared to ≤ 1 mmol L^{-1} for glucose, for example[54,55].

The first lactate-oxidizing buckypaper bioanode was developed by Atanassov and coworkers. Commercial MWCNT buckypaper (Buckeye Composites) was modified with methylene green as an electrocatalyst to regenerate dissolved NAD^+ cofactor, chitosan as a biocompatible stabilizing matrix, and adsorbed lactic dehydrogenase (LDH) from *Lactobacillus leichmannii* as the selective catalyst[56]. The bioanode was not tested in a fuel cell setup but could potentially be exploited. However, the catalytic current of 53.4 ± 5.1 μA cm^{-2} in buffer solution is low and the need to add the enzyme's cofactor are major limitations.

A practical lactate-oxidizing bioanode integrated into a hybrid photoelectric biofuel cell was recently reported by Dong and coworkers. In this work, MWNCT buckypaper (Buckeye Composites) was modified with Meldola blue, chitosan, and lactate oxidase (LOx) *from Pediococcus sp*[11]. In addition to serving as a redox mediator, the pi-pi stacked Meldola blue molecules on the CNTs shifted the buckypaper surface wettability from hydrophobic (<100°) to hydrophilic (<30°). The hydrophilicity is attractive to promote enzyme adsorption, during modification, and contact with electrolytic solution, during operation. The bioanode delivered high catalytic current densities of *ca.* 2.1 mA cm^{-2} in buffer solution and was successfully integrated into a wearable epidermic lactate/O_2 biofuel cell capable of powering a Bluetooth module and transmitting data to a smartphone (Figure 1.3).

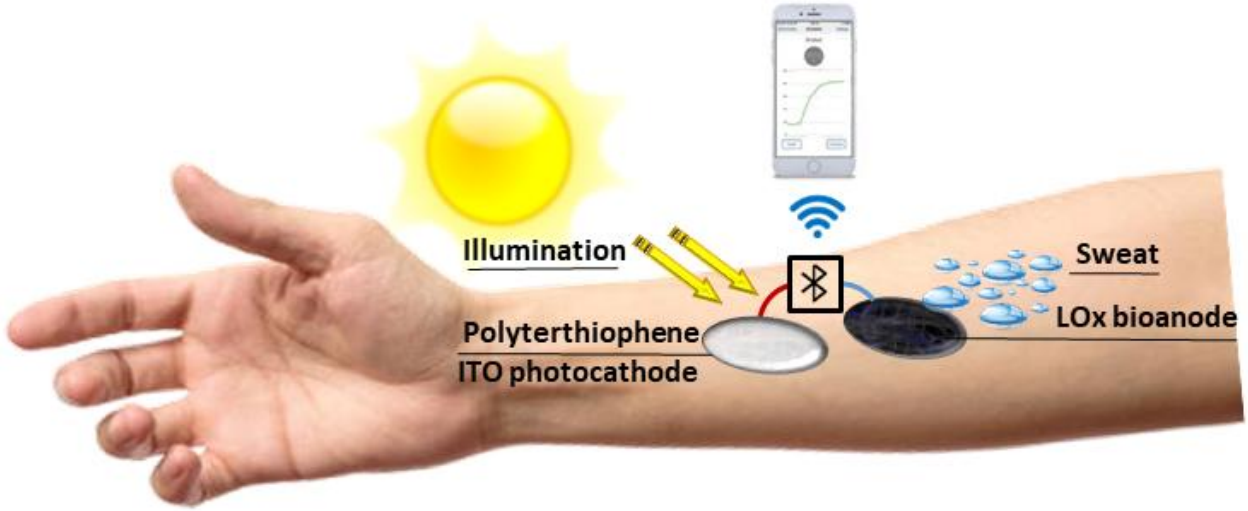

Figure 1.3: Principle of a wearable hybrid biofuel cell with a polyterthiophene-coated indium tin oxide photocathode and a lactate-oxidizing buckypaper bioanode.

Buckypaper bioelectrodes have also been developed for energy harvesting from tear fluid to power 'smart' electronic contact lenses for applications in human vision and sensing[18]. It is envisioned that such biofuel cells could be used to power contact lenses worn by type I diabetics for non-invasive glucose monitoring[57]. Minteer and coworkers exploited commercial MWNCT buckypaper (Buckeye Composites) immobilized on an elastomeric contact lens[18]. Buckypaper was used to benefit from its high surface area, laser cuttability, durability and mechanical properties such as flexibility. For example, the authors reported that the buckypaper exhibited better mechanical properties compared to other conductive papers such as Toray paper and evaporated metal electrodes. The bioanode was constructed with NAD-dependent lactate dehydrogenase (NAD-LDH) *from Escherichia coli* modified

with methylene green electrocatalyst and a cross-linked polymeric hydrogel matrix to entrap the NAD^+ cofactor and enzyme on the electrode surface. The use of immobilized NAD^+ is in principal more practical than the classical approach that requires cofactor to be added to the solution. A further advantage is that this strategy could be applied to a wide range of NAD-dependent enzymes. In addition to lactate oxidation, electrocatalytic ascorbic acid oxidation was also observed, although this had parasitic effects on the fuel cell. Lisdat and coworkers also observed parasitic effects due to ascorbic acid oxidation at buckypaper electrodes in human biofluids[19]. For the biofuel cell developed by Minteer and coworkers, the lactate-oxidizing bioanode was combined with an oxygen-reducing biocathode prepared via oriented adsorption of bilirubin oxidase (*Mv*BOx) on pyrenemethyl anthracene modified buckypaper. The biofuel cell delivered an OCV of 0.41 V and a small power output up to 8 $\mu W\ cm^{-2}$ at 0.2 V in tear solution with stability for several hours[18]. The low power output and stability revealed that there is plenty of room for improvement. Improved performance could be achieved by removing the ascorbic acid interference, increasing the amount and stability of the immobilized enzymes and cofactor, and by reducing biocatalyst leaching.

The mechanical and chemical properties of buckypaper can also be improved for wearable and implantable applications. The strength and Young's modulus of buckypaper electrodes can be enhanced by incorporating functional polynorbornenes[58] and molecular cross-linkers such as pyrene derivatives[22,33]. The introduction of polynorbornene copolymers, as illustrated in Figure 1.4, revealed the possibility to introduce multiple functionalities to the buckypaper, such as pyrene groups, for cross-linking, and a reactive *N*-hydroxysuccinimide ester, for covalent tethering of molecules for enzyme wiring or the enzymes themselves[58]. Alternatively, the strength, properties and hardness of buckypaper can be significantly enhanced by aligning the CNTs in the buckypaper with a high packing density[15]. Lab-made rather than commercial buckypapers may hold the key to improved buckypaper biofuel cell performance, for example, due to (i) the ability to better tune the chemical and physical properties of the bulk materials, (ii) their superior larger surface areas, and (iii) their apparently improved enzyme wiring for bioelectrocatalysis[6,16].

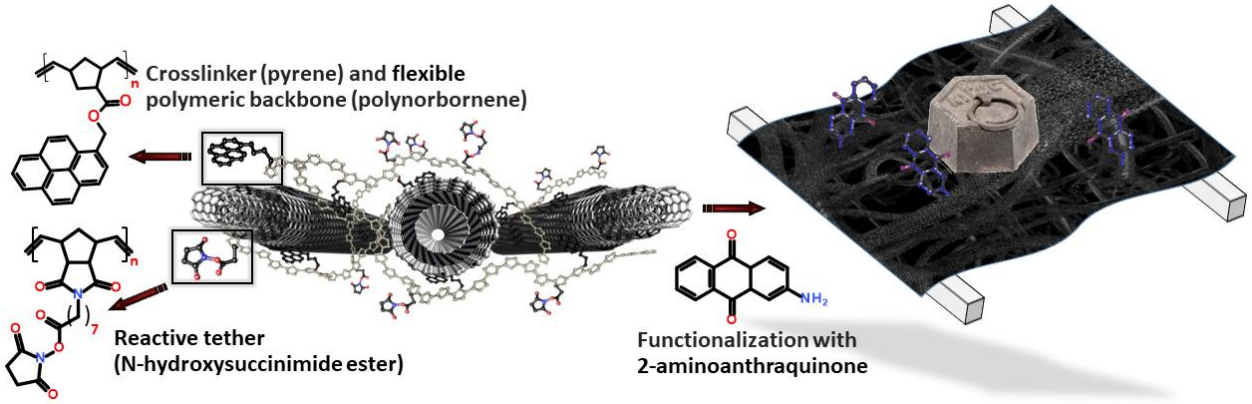

Figure 1.4: Incorporation of 'precision' polynorbornenes in buckypaper to improve the mechanical properties, such as flexibility, tensile modulus and strength, and the chemical properties, for covalent attachment of molecules to improve enzyme orientation and wiring.

1.2.3 Portable enzymatic biofuel cells

Enzymatic glucose/O_2 biofuel cells have been designed for powering of portable electronics such as music players and toy cars[59]. One potentially exciting application is the development of eco-friendly paper-based power sources. Atanassov and coworkers initiated the development of MWCNT buckypaper-based paper biofuel cells that delivered up to 1.8 V (3 biofuel cells in series) and power outputs up to 13.1 mW under quasi-steady flow[60,61]. In one example, a digital clock was powered using the commercial soft drink, Gatorade, which was supplied via cellulose filter paper. In addition to demonstrating the portable paper-based biofuel cell concept (using buckypaper from Buckeye Composites), this work nicely demonstrated the possibility to use commercially-available liquids rather biofluids or environmental matrices to generate power. The need to add NAD^+ cofactor for glucose oxidation at the NAD-dependent glucose dehydrogenase (NAD-GDH) anode is nevertheless a significant inconvenience[60]. In later work by the authors, the same bioanode was combined with an air-breathing MWCNT buckypaper/Toray paper composite modified with *Mv*BOx as the oxygen-reducing biocathode[61]. This paper biofuel cell also benefited from a supercapacitive element that facilitated the production of mW power outputs, under pulse operation, and 4200 discharge/recharge cycles over a period of 3 days[61].

The elegant concept of using cellulose paper as a transport medium to induce passive flow via wicking has also been explored for construction of a paper-based "enzyme cascade"-based biofuel cell. This novel type of biofuel device was developed to improve bioanode performance by exploiting sequential catalytic reactions and multiple fuels (Figure 1.5). Multiple NAD(H)-dependent enzymes

were used at the MWCNT buckypaper (Buckeye Composites) anode for the multi-step oxidation of ethanol to acetate, and complete oxidation of methanol to CO_2[62].

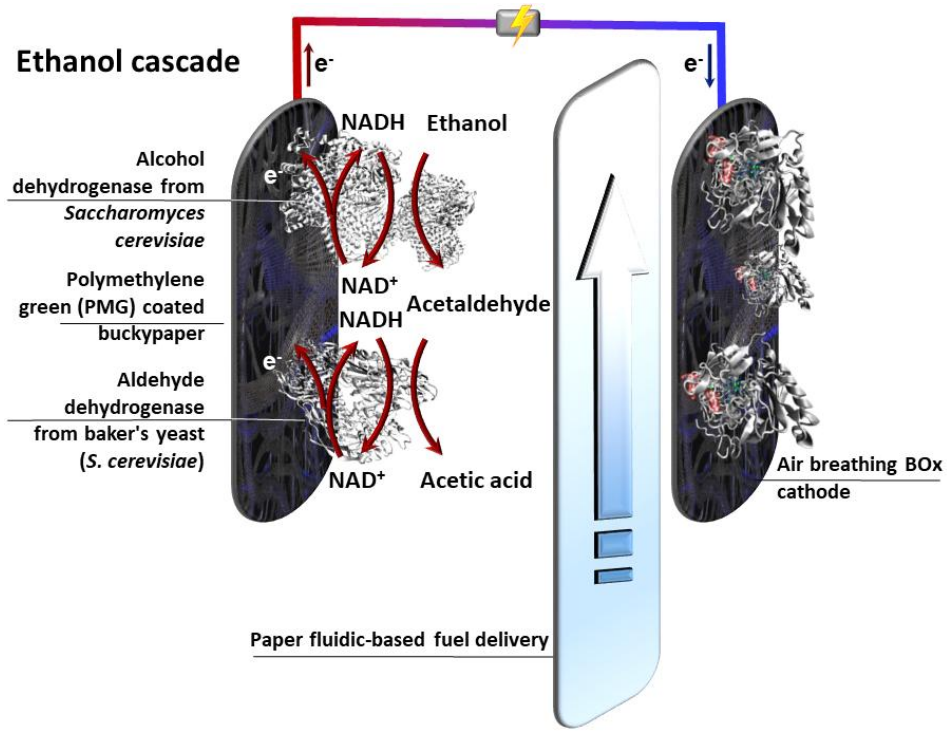

Figure 1.5: Schematic of a biofuel cell with a multiple NAD-dependent enzyme bioanode, for the cascade oxidation of ethanol to acetic acid, coupled with an air-breathing BOx biocathode, for oxygen reduction. The fuel ethanol is delivered to the cell via paper fluidics.

The ability to use air-breathing cathodes is a major advantage for portable biofuel cells compared to in-vivo biofuel cells due to the possibility to enhance oxygen delivery at the electrode interface. The testing and optimization of MWCNT buckypaper-based air-breathing biocathodes with immobilized *Mv*BOx has been reported[63,64]. As well as air-breathing cathodes, the use of glucose-oxidizing anodes which exploit the emerging enzyme, FAD-dependent glucose dehydrogenase (FAD-GDH), is considered to be one of the most practical biofuel cell setups currently available. The use of FAD-GDH, which is oxygen insensitive (unlike glucose oxidase) and can now be obtained commercially, has only very recently reported in combination with quinone-modified buckypapers, and promisingly, gave high catalytic currents up to 1.97 $mAcm^{-2}$ [65] and 5.4 mA cm^{-2} [6]. The integration of an FAD-GDH-based buckypaper anode in biofuel cells was reported but not yet in combination with an air-breathing cathode.

The integration of energy storage elements such as supercapacitors together with biofuel cell stacks, assembled in series or parallel, is expected to become increasingly important for the powering

of portable miniaturized electronic devices[10]. Hou and Liu reported a flexible lab-made buckypaper biofuel cell device connected in series based on a FAD-GDH modified anode and a laccase modified cathode. In addition, a supercapacitor was incorporated based on polyvinylalcohol (PVA)-H_3PO_4 and a MWCNTs-polyaniline composite[10]. The self-charging device delivered a charging voltage of 0.8 V and a power density up to 326 μW cm^{-2} (a two-fold increase in power compared to the biofuel cell without the supercapacitor). The capacitance of the MWCNTs/polyaniline electrode was observed to be 329 F g^{-1} at 10 mVs^{-1}. For comparison, Tran *et al.* reported a potentially better-performing supercapacitor based on the in-situ electropolymerization of polyaniline at buckypaper (397 Fg^{-1} at 10 mV s^{-1})[66]. Furthermore, Gross *et al.* observed clear performance differences with FAD-GDH based bioanodes with different mediators[6]. For example, it was demonstrated that around a 5-fold improvement in catalytic current density can be achieved by changing from a naphthoquinone (NQ) to a phenanthroline quinone (PLQ) derivative. Nevertheless, the NQ buckypaper showed advantages such as a slightly lower onset potential and the possibility to reach the catalytic current plateau at lower potentials compared to the PLQ buckypaper. The buckypaper biofuel cell with a powerful PLQ bioanode for glucose oxidation is illustrated in Figure 1.6. Examples of the bioelectrocatalytic cyclic voltammograms recorded during half-cell characterization are also shown in Figure 1.6.

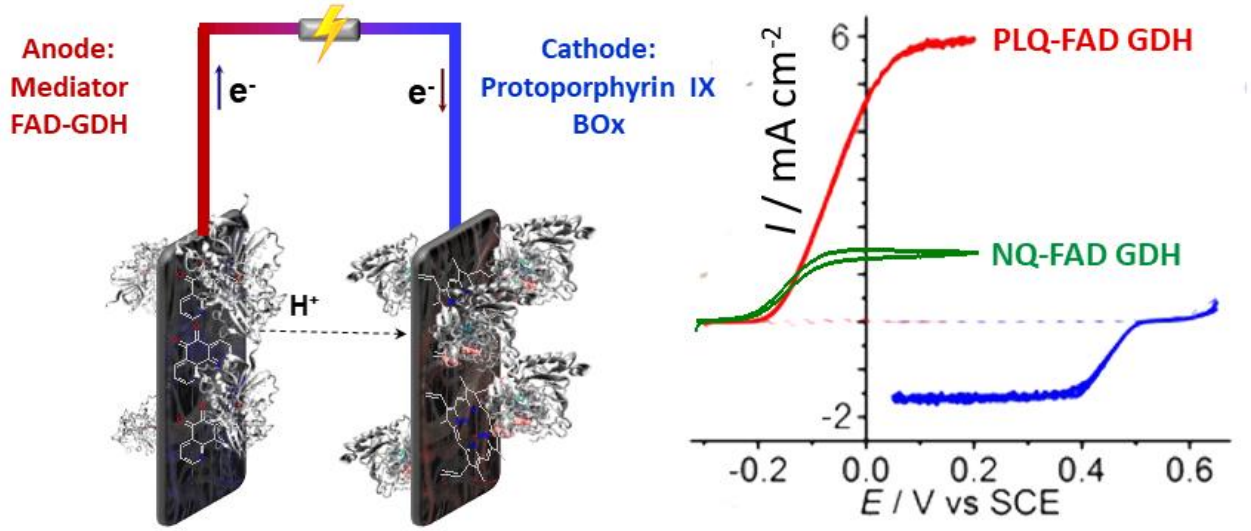

Figure 1.6: Cartoon of the buckypaper-based glucose/oxygen biofuel cell using FAD-GDH and an artificial quinone mediator at the bioanode, and protoporphyrin IX-oriented BOx at the biocathode. Right: cyclic voltammograms of bioelectrocatalysis at FAD-GDH bioanodes, with different mediators (PLQ) and (NQ), and the BOx biocathode.

Enzymatic biofuel cells have also been explored as portable, low-temperature and sulfur-insensitive alternatives to solid oxide fuels cells that run on JP-8 jet fuel, for example, for military applications. Minteer and coworkers exploited an enzyme cascade of alkane monooxygenase (AMO) and alcohol oxidase (AOx) at a MWCT buckypaper (Buckeye Composites) anode for mediated bioelectrocatalytic oxidation of hexane, octane, and jet fuel[67]. This study demonstrated the possibility to exploit alkanes as fuels for biofuel cells for the first time, and additionally, showed the possibility to produce power densities up to 3 mW cm^{-2} without pre-processing of alkane-based fuels.

1.2.4 Microbial biofuel cells

Microbial biofuel cells which exploit electroactive microbes such as bacteria are an eco-friendly technology for applications such as energy-generating wastewater treatment, self-powered sensors, and large scale electricity production from biomass[68,69]. Compared to enzymatic biofuel cells, microbial biofuels typically give lower catalytic efficiencies but are better suited to large-scale energy generation and therefore larger raw power output. Bioelectrodes based on bacteria are also generally more durable under harsh and polluted conditions compared to enzymatic electrodes. A typical microbial biofuel cell consists of an anode with acidophilic bacteria on the electrode surface, for oxidation via metabolic processes, and a cathode, typically Pt or activated carbon, for oxygen reduction. The anode and cathode are classically placed in individual chambers and separated by an ion selective membrane.

In 2013, Santoro, Atanassov, Ieropoulos and coworkers reported for the first time the use of a microbe-based carbon cloth anode together with a MWCNT buckypaper (Buckeye Composites)-carbon cloth enzymatic air-breathing cathode in a compartmentless hybrid biofuel cell[9]. The biofuel cell operated in buffer with additional sodium acetate and wastewater solutions. A key observation was that the biofuel cell exploiting the oxygen-reducing BOx modified cathode exhibited a *ca.* 200 mV improvement in OCV compared to the biofuel cell with a Pt cathode under equivalent conditions. A maximum power density of 2 W m^{-2} (200 μW cm^{-2}) was achieved in 125 mL of buffer solution.

A hybrid microbial biofuel cell was also developed and tested in both laboratory and marine environments. The carbon felt microbial anode was prepared with silica-encapsulated *Shewanella oneidensis* DSP-10, for lactate oxidation, and an oxygen-reducing MWCNT buckypaper (Buckeye Composites) cathode modified with either laccase or BOx via 1-pyrenebutyric acid N-hydroxysuccinimide ester (PBSE) cross-linking[70]. Unlike the previous report from *Santoro et al.*, this hybrid biofuel cell used individual anode and cathode compartments separated by a polycarbonate membrane[9]. The biofuel cell, depicted in Figure 1.7, was tested in seawater and delivered 0.7 V for 9

days and 0.95 W m^{-3} (22.4 μW) using the best performing buckypaper biocathode based on BOx. Towards real-world applications, the biofuel cell device was also tested in a marine environment using a floating watercraft.

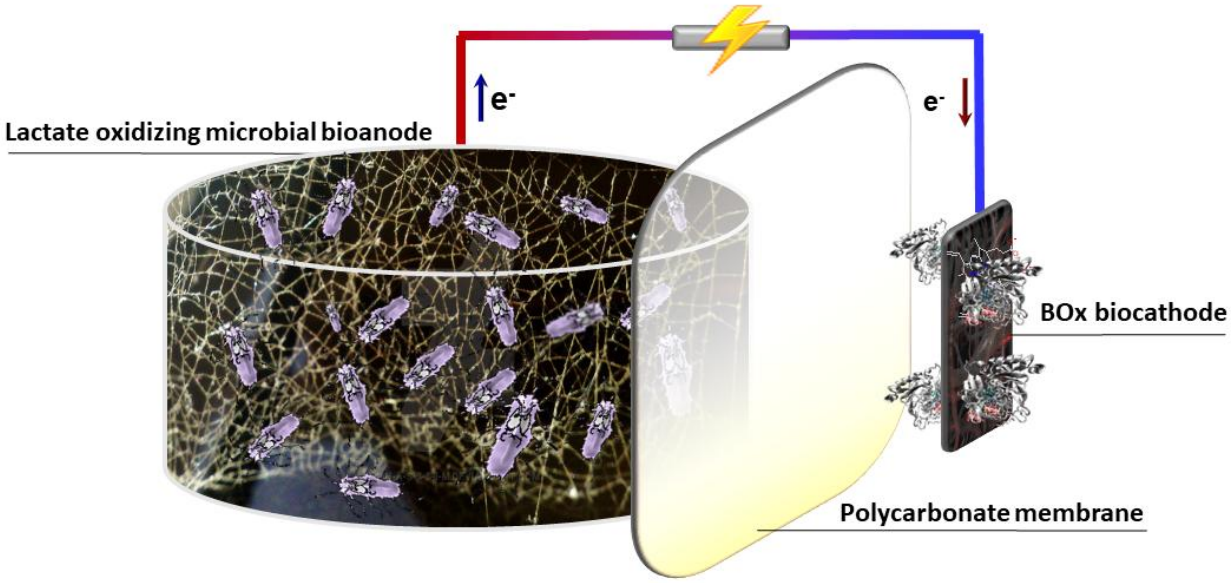

Figure 1.7: Representation of a hybrid microbial biofuel cell for harvesting energy from sea water with an enzymatic cathode and a microbial bioanode in individual compartments.

To improve power performance for portable wastewater applications, Santoro, Atanassov and coworkers reported a "smart" supercapacitive microbial biofuel cell[71]. The fuel cell was designed with an air-breathing MWCNT buckypaper (Buckeye Composites) cathode modified with BOx, and an activated carbon/carbon black microbial anode with a mixed cultures bacteria. In addition, a carbon brush supercapacitor electrode was short-circuited to the microbial anode. The supercapacitive fuel cell delivered up to 19 mW (84.4 W m^{-2}, 152 W m^{-3}) at pulse currents as high as 45 mA, which is one of the highest power values reported for a microbial fuel cell. The authors highlighted that the integrated capacitor exhibited shorter recharging times (seconds to minutes) compared to the use of external supercapacitors (hours). Having shorter recharge times is attractive due to the possibility to increase the power output frequency. A further advantage is that the supercapacitor size can be modulated to de-couple energy and power depending on the target application.

Buckypaper has also been explored as a high surface area conductive support for the preparation of microbial anodes in biofuel cells[72,73]. Kerzenmacher and coworkers reported a comparison of bioanodes modified with *Shewanella oneidensis* MR-1 and prepared using different carbon materials; namely, activated carbon felt and cloths, graphite felt and foil, Toray paper, and lab-made MWCNT

buckypaper. The high surface area activated carbon cloth with a Brunauer-Emmett-Teller (BET) specific area of *ca.* 800 m^2 g^{-1} outperformed the other carbon materials in terms of catalysis per geometric area and also OCP due to factors such as improved mass transport, electron transfer (e.g. mediated electron transfer via self-secreted flavins), and bacterial migration into the porous structure (e.g. enhanced catalyst loading). Nevertheless, the buckypaper exhibited the largest catalytic current in terms of the volumetric density. Volumetric density is arguably a more accurate representation of current density due to the 3D nature of the electrodes. Lower ohmic losses were also observed using buckypaper, attributed to the enhanced conductivity of CNTs. The lab-made MWCNT buckypaper reported in this work had a BET surface area of 70 m^2 g^{-1} which compares to values of *ca.* 30 and 260 m^2 g^{-1} reported recently by us for commercial (Buckeye Composites) and lab-made MWCNT buckypaper electrodes[16]. In a 2018 study, Kerzenmacher and coworkers reported a systematic comparison of bioanodes with the prominent model organism, *Geobacter sulfurreducens*[73]. Similar catalytic current densities were observed at different carbon and metal-based anodes, which included lab-made MWCNT buckypaper. The highest limiting current density of up to 756 μA cm^{-2} was observed with graphite foil, which compares to the 613 μA cm^{-2} observed when buckypaper was used. In terms of the time until the limiting current is reached, buckypaper anodes took *ca.* 319 hours whereas graphite foil took *ca.* 1134 hours (including the one week initial growth phase) using step-wise galvanostatic characterization.

1.3 Biosensors

Biosensors which employ glucose-oxidizing enzyme electrodes are devices that have already shown success in the form of electrochemical glucose biosensors for diabetes management[74]. Enzymes are attractive for biosensing owing to their exceptional substrate selectivity, high specific activity per active site, and inherent biocompatibility. The development of implantable and wearable biosensors offers the ability to continuously monitor physiological analytes with minimal patient intervention and to provide real-time health information[75,76]. Future wearable biosensors will be non-invasive or minimally-invasive devices and therefore (i) avoid the need for surgery and (ii) reduce complications associated with biocompatibility. The realization of wearable sensors is therefore more tangible than implantables. To date, wearable sensors have been almost exclusively developed for monitoring physical physiological parameters such as skin temperature, heart rate and pressure[75]. For the development of wearable electrochemical sensors, electrode materials are required that are soft, flexible and stretchable (e.g. mechanical properties similar to human skin), as well as being

lightweight and having large surface areas. Buckypapers and their composites can offer these types of properties.

Minteer and coworkers developed a self-powered amperometric lactate biosensor based on LOx from *Pediococcus sp* cross-linked onto a MWCNT buckypaper modified with a Fc-based polyethylenimine polymer hydrogel[4]. The authors reported that the flexibility of buckypaper and its ability to adhere to non-planar surfaces during repeated bending was attractive for the envisaged lactate skin patch and contact lens sensors. The amperometric lactate biosensor based on mediated electron transfer exhibited a detection limit of 1 μmol L^{-1}, a calibration range up to 40 mmol L^{-1}, and storage stability up to 21 days. In addition, the biosensor was stable in the presence of ascorbate, a common interference present in biofluids.

Ahmadalinezhad *et al.* developed a buckypaper-based biosensor platform using a gold-coated titanium substrate as a mechanical support[77]. Buckypaper was electrochemically functionalized with carboxylic acid groups then modified by adsorption of GOx *from Aspergillus niger*, horseradish peroxidase (HRP) and chitosan to complete the sensor. Amperometric glucose detection was indirectly monitored at 0.1 V vs AgAgCl based on the reduction of H_2O_2 produced by the enzymatic oxidation of glucose. The mediatorless glucose biosensor demonstrated high selectivity in the presence of common interferents (ascorbic acid, uric acid and acetamidophenol), a dynamic range of 0.01 to 9 mmol L^{-1}, sensitivity of 20 μA mmol L^{-1} cm^{-2}, and a long lifetime of over 80 days. The excellent stability was attributed to the physical and chemical properties of the buckypaper combined with the use of chitosan for enzyme stabilization.

Chatterjee and Chen subsequently reported a buckypaper-based biosensor for the determination of H_2O_2 in urine for monitoring of oxidative stress in-vivo[12]. The same buckypaper-titanium substrate was used as reported previously[77], followed by electrochemical surface oxidation, and immobilization of HRP, chitosan, and the mediator methylene blue. A low detection limit of 7.5×10^{-8} M, a dynamic range of 0.1 to 500 μmol, and a sensitivity of 54 μA mmol L^{-1} cm^{-2} were reported. Spike recovery analysis revealed recoveries of 95-105% in human urine, demonstrating the validity of the method as an in-vivo biosensor.

Decoration of CNT buckypapers with nanoparticles can be used to improve conductivity,[78] mechanical[79] and catalytic performance[80,81], and enzyme wiring via electronic bridging or electron mediation[82,83]. Papa *et al.* developed a glucose biosensor based on lab-made acid-treated SWCNT and MWCNT buckypapers prepared in the presence of citrate-capped gold nanoparticles[84]. A schematic showing the construction of the sensor mechanism is shown in Figure 1.8. GOx enzyme, HRP and chitosan were subsequently cast onto the buckypaper to generate the bioelectrode. The SWCNT BP

with embedded gold nanoparticles exhibited the best performance with a dynamic range of 0.02 to 7 mmol L^{-1}, sensitivity of 21.5 μA mmol L^{-1} cm^{-2}, and no significant response from physiological interferents (ascorbic acid and uric acid). More recently, the same authors expanded the development of the gold nanoparticle-modified SWCNT and MWCNT buckypapers for the electrochemical detection of biologically important molecules such as tryptophan, L-carnitine, tyrosine, and myoglobin with 1000-fold increase in the signal in buffer compared with classical glassy carbon electrode sensors[85,86]. For the myoglobin sensor, methylene blue was integrated into the buckypaper to facilitate electron transfer between the electrode and the protein's active site. The reported patent covers methods for the construction of functionalized buckypaper biosensors as an alternative to the use of screen-printed and glassy carbon based electrodes[86]. It is noted that the specificity of the GOx-gold nanoparticle-based biosensors in the presence of interferences was not demonstrated.

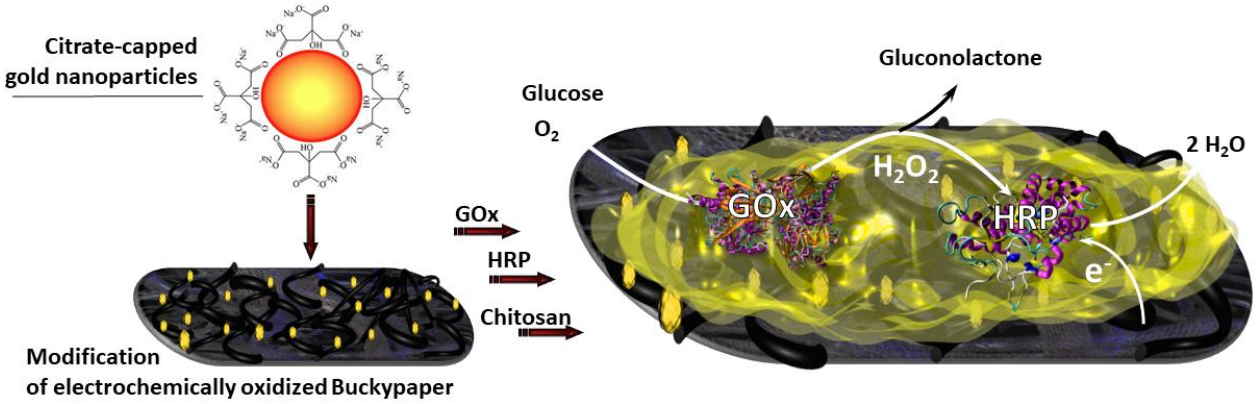

Figure 1.8: Scheme showing the fabrication of a buckypaper-based biosensor for the indirect detection of glucose. The electrochemical signal is generated by the electrocatalytic reduction of H_2O_2, produced by GOx after oxidation of glucose via HRP.

As an alternative to enzyme-based biosensing, the work of Desai *et al.* demonstrates the successful application of a lab-made MWCNT buckypaper as an electrical nanosensor on a printable circuit. The non-enzymatic bioelectrode sensor was constructed by immobilization of single stranded DNA and used to monitor DNA-hybridization of pathogen DNAs based on device resistance changes resulting from the wrapping and unwrapping of DNA[87,88].

1.4 Biosynthesis

An exciting and largely unexplored application of buckypaper electrodes is in the field of electroenzymatic synthesis. Enzymes offer attractions compared to chemical catalysts such as high

selectivity and reaction rates under eco-friendly conditions, and are therefore recognized as powerful catalysts in industrial biotechnology, for example, for the generation of pharmaceuticals and fine chemicals including enantiomerically pure compunds[89]. Etienne, Walcarius and coworkers have made progress on an electroenzymatic "reactor" concept, for example, for the regioselective conversion of D-sorbitol into D-fructose at an appreciable rate[90]. An activated carbon/MWCNT bioanode was modified with polymethylene green and NAD-dependent D-sorbitol dehydrogenase (DSDH) for catalytic sorbitol and NADH oxidation. The substrate and NAD^+ cofactor were flowed continuously into the reactor during operation. More recently, Etienne and coworkers developed a new catalytic bioelectrode design based on buckypaper for electroenzymatic synthesis[13]. Lab-made MWCNT buckypaper was elegantly modified with a Rh complex catalyst via diazonium surface chemistry and used for efficient NADH regeneration during sorbitol synthesis via the enzyme DSDH (Figure 1.9). The work constitutes significant advances in terms of reusability, good catalytic activity for NADH regeneration (turnover frequency of 1.3 s^{-1}), and efficient conversion over several days (conversion rate of 87% after 95 h).

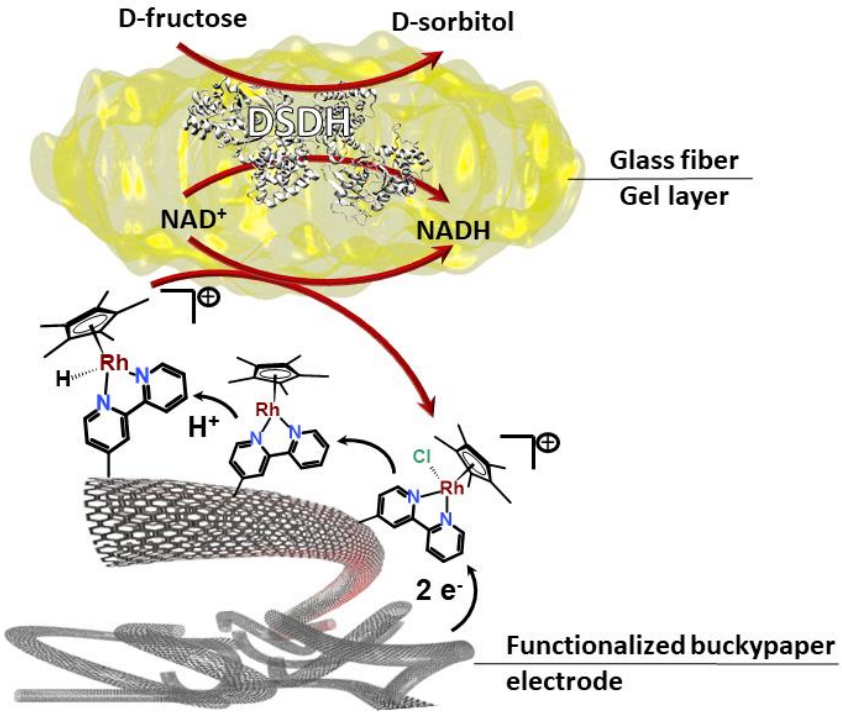

Figure 1.9: Schematic representation of the bioelectrocatalytic synthesis of sorbitol from fructose using a Rh complex for the regeneration of NAD and the enzyme catalyst, sorbitol dehydrogenase (DSDH).

1.5 Biologic

Buckypaper bioelectrodes also offer interesting possibilities in which their biocatalytic reactions may be used for biocomputing, for example, for novel multi-signal sensor applications. The review of Katz and Privman serves as an excellent introduction to this topic[91]. Strack *et al.* demonstrated for the first time that buckypaper bioelectrodes could be used for sustained built-in information processing[14]. A direct electron transfer biocathode configuration was used in which a laccase-based MWCNT buckypaper (Buckeye Composites) responded directly to dissolved oxygen, as a continuous input signal, and could generate an amperometric response, as the output signal. Nitrogen and oxygen were pumped into a flow system to give stable and reproducible current signals at an applied potential of 0.4 V over more than 100 cycles and a 20 day period. The current output with nitrogen served as "on" or "1" and with oxygen served as "off" or "0". The device was used to generate a binary-based code sequence (ASCII 12-bit Code 39) that could be read by a conventional barcode scanner. This proof-of-concept study ultimately demonstrated the prospect of using biocatalytic buckypapers for responding to incoming signals, processing them, and relaying them ex-vivo. Use of signals from substrates present in biological fluids such as sugars and oxygen would open up the prospects for in-vivo data processing.

1.6 Conclusion

Buckypaper materials based on carbon nanotubes have witnessed great success for the construction of bioelectrodes based on enzymes and microbes owing to a unique combination of properties such as their high conductivity, mechanical strength and flexibility, lightweight, and their porous high surface area structures. Both lab-made and commercial buckypapers have proved to be practical supporting frameworks for enzymes and catalytic components including nanoparticles and non-metal catalysts, as well as functional building blocks including polymers and cross-linking molecules. A wide range of functional catalytic biointerfaces have been reported over the last 5 to 7 years for applications including bioenergy conversion and storage (enzymatic and microbial biofuel cells, hybrid biofuel-capacitor systems, and photoelectric biofuel cells), chemical and biochemical detection (enzymatic and non-enzymatic biosensors), and information processing devices (biologic systems). The greatest achievement of buckypaper to date has been its use in *actual* implanted biofuel cells for energy-harvesting from organisms such as snails and lobsters; no other electrode can boast as much success in the field of biological fuel cells. There is still a huge amount of work to be done to improve the performance of implantable and wearable biofuel cells, and we note in particular the importance of evaluating the stability, biocompatibility and toxicity of buckypaper bioelectrodes in future studies.

Until now, the majority of reported buckypaper bioelectrodes have been prepared using commercial buckypaper from Buckeye Composites, and this type of readily available buckypaper has proved to be an excellent electrode platform. We nevertheless envisage a bright future for lab-made buckypaper electrodes that can be prepared using relatively straightforward procedures in the laboratory, and which permit a higher level of control over the physical, chemical and catalytic properties of the electrode. We also recognize that a wide variety of parameters affect the performance of lab-made buckypaper and thus we take this opportunity to emphasize the importance of providing accurate details with respect to the fabrication methods and materials used for buckypaper preparation. With all of this in mind, there should be little doubt that buckypaper will continue to play an important role not only for the construction of future bioelectronic devices but also for other applications in the fields of electrochemistry, energy, and materials science.

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