Multimaterial Fibers for Biosensing Application Using Electrochemistry

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science
In
Electrical Engineering

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June 1st, 2021
Blacksburg, Virginia.

Keywords: biosensors, electrodeposition, sensing, electrochemical, fibers, multimaterial

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ABSTRACT

The biosensing field has grown in importance and research efforts over the last few years for many reasons including point of care sensing devices and possible early detection of diseases in the body. Dopamine sensing is discussed in this paper and development of a dopamine sensing platform would lead to early detection of diseases linked to its abundance or lack thereof in the brain such as Parkinson's disease. This work focuses on the electrochemical methods of biosensing, specifically dopamine sensing, and this method involves the use of electrodes as its sensing component. Multimaterial electrode-embedded fibers are used as the sensing electrode and the electrode material presented is platinum (Pt). Platinum is employed because of its biocompatibility property. The electrodes are placed in the fiber by method of convergence fiber drawing and the fiber ends are stripped to expose the electrode for application. To make the proposed sensing platform more cost-effective, the platinum is electrodeposited onto the multimaterial fiber's embedded electrode. We discuss the use of a W/Pt modified electrode and a pure platinum wire in dopamine sensing, and demonstrate that Pt is indeed a good candidate for dopamine sensing. The results show that the sensitivity of the W/Pt modified electrode to dopamine is higher than that of a pure Pt wire. This work has shown the promising application of electrodeposition in developing a cheaper flexible biosensing platform, and opens up the possibility of the development of wearable flexible smart textile sensors because of the use of flexible multimaterial fibers.

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GENERAL AUDIENCE ABSTRACT

The idea of sensing is important to our world and various scientific developments in this area have improved our way of life as humans. Biological sensing, which is what this thesis focuses on, detects the presence of various substances in the body and developments in the area of biosensing have led to the creation of devices that can detect diseases or gather general information about a person's anatomical state. There has been increased interest in the detection of dopamine as more studies show that some diseases such as Parkinson's disease are related to the amounts of dopamine present in the brain. In this work, we present a potential platform for sensing dopamine in vitro using electrochemistry. Multimaterial fibers with embedded electrodes capable of measuring dopamine were fabricated using a thermal drawing technique. The electrode material in this fiber is the most important part of the sensing platform as it is what determines how sensitive the fiber is to an analyte. The two main topics discussed in this work are the modification of the electrode material using an electrodeposition technique and the sensing of dopamine with the modified electrode using the electrochemical methods of cyclic voltammetry and differential pulse voltammetry. The material involved in the electrodeposition process is Platinum (Pt) and the results show that platinum is a suitable material for dopamine sensing.

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CHAPTER 1- Introduction

Biosensor related research has grown over the last two decades. Today, about 4500 papers are published on biosensors each year, and worldwide sales of biosensors are about $13 billion[1]. Figure 1-1, gotten from the cited paper [1], shows the estimated past, present, and future world market for biosensors. A biosensor can be defined as a device that converts a biological response inside or outside the body into a quantifiable and processable signal. Figure 1-3 below shows the components of a biosensor. Biosensors can be applied to a wide variety of samples such as body fluids, food samples, cell cultures, and have also been used to analyze environmental samples[2], [3]. It would be remiss talking about biosensors without reflecting on their origin and founding fathers. The early era of biosensing research was kicked-off by the late Leyland C. Clark and his invention of the oxygen electrode in 19955/66[4]. This oxygen electrode was modified and this modification led to another paper in 1962 that reported the development of the first glucose sensor. Clark's work and his technology were subsequently transferred to Yellow Spring Instrument Company, and this led to the successful commercial launch of the first glucose biosensor in 1975[5].

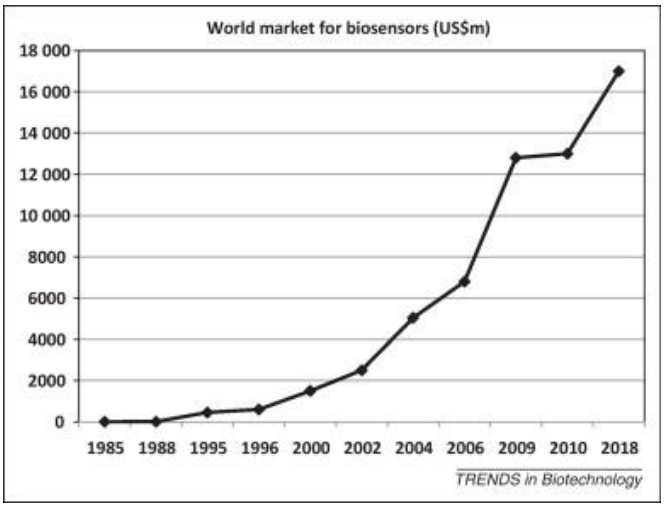

Figure 0-1: Estimated past, present, and future world market for biosensors[1]

An interesting biosensor invention that emerged in the 1980s is the 'Bananatrode'[6]. The bananatrode is an electrochemical biosensor that senses dopamine. According to Sidwell et al., the sensor uses a Clark-type oxygen electrode in conjunction with banana pulp tissue slices that serve as a biocatalyst for the quantification of dopamine. The principle of the sensor is based on the browning reaction of a banana. The enzyme polyphenol oxidase catalyzes the oxidation of dopamine to quinone, and this reaction consumes oxygen. The oxygen consumption in this reaction results in an electrical signal via the oxygen electrode, and the electrical signal is proportional to the concentration of dopamine present. Figure 1-2 depicts a schematic diagram of the electrode assembly[6].

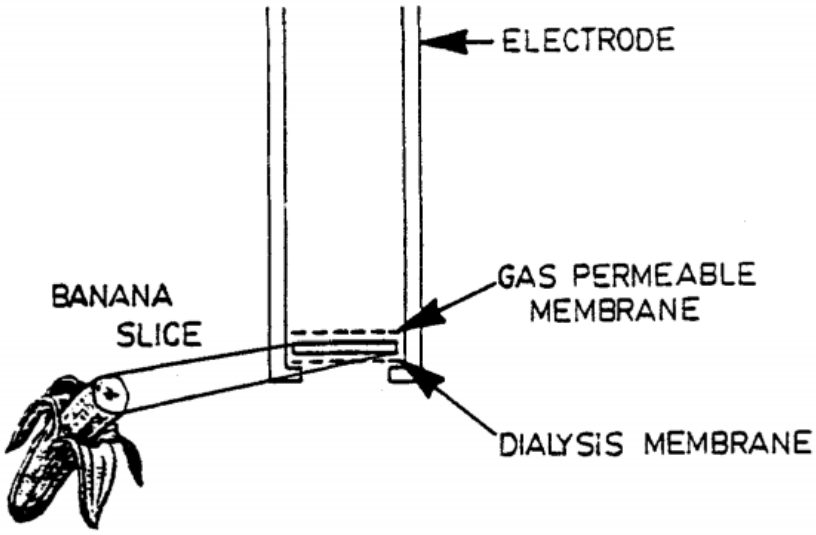

Figure 0-2: Schematic of 'Bananatrode' electrode setup

Biosensors detect the presence of biological analytes such as cells, protein, biomolecules, or a microorganism [7]. According to nature research, biosensors consist of three parts; a part that recognizes the analyte and produces a signal (also called bioreceptor), a signal transducer, and a reader device [8]. Bioreceptor examples include enzymes, antibody, DNA, cells, tissues, biomimetics[9]. The bioreceptors interact with the analyte to produce a signal or response, and the transducer is the biosensor component that converts a biological response to an electrical signal for reading and processing [10]. A transducer could be optical[11], electrochemical, magnetic[12], [13], thermometric/thermal[14], [15] or piezoelectric[16]. The various types of transducers reflect how the material in the transducer converts the biological response into an electrical signal e.g. an optical transducer would use light in sensing an analyte or a magnetic transducer would utilize a magnetic field. Each transducer type also corresponds to a certain type of biosensing method. The sensing properties of a biosensor depends on the transducer material, where some materials have better sensitivity and/or selectivity for specific analytes or bioreceptors than others. In most biosensing discoveries or projects today, the surface of the sensing material is normally modified or functionalized to increase its sensitivity towards the sensed analyte. The different biosensing methods produce different results, and they have some advantages and disadvantages over each other. Some biosensing methods can also be combined to increase the effectiveness of the sensor, combine the advantages of multiple methods and create multifunctional biosensors. For example, Eltzov et al. reviews the development of biosensors based off of combined optical and electrochemical transduction methods for molecular diagnostics[17]. When biosensor development is discussed, the features that are highlighted include sensitivity, specificity, and cost-effectiveness. In the following paragraphs, we present various biosensing methods and expatiate on them.

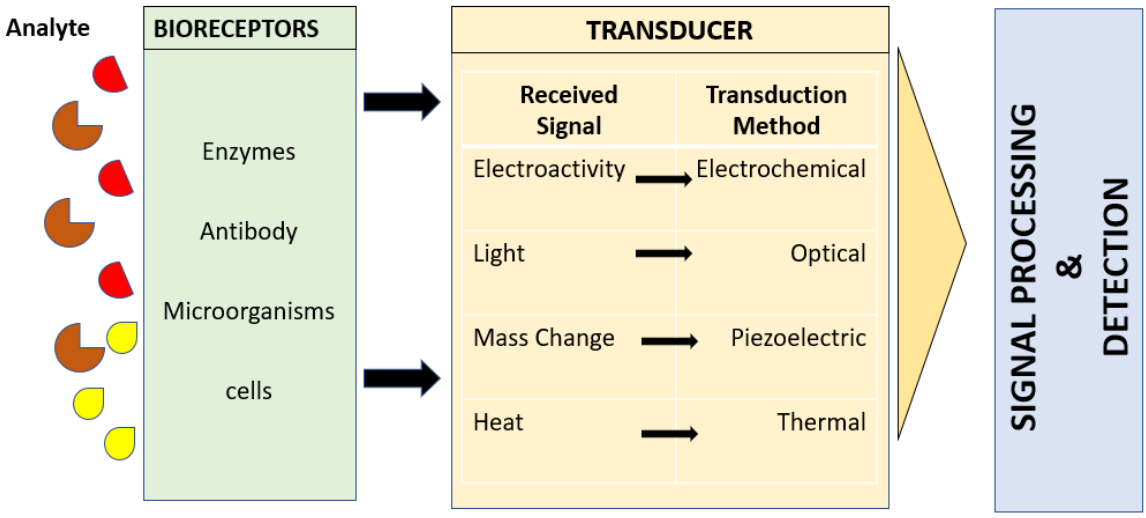

Figure 0-3: Components of a Biosensor (compiled from [18]–[21])

1.1 Biosensing Methods

Electrochemical sensors are a class of sensors where an electrode is the sensing element or transducer. The electrode surface is where reaction with the analyte or bioreceptor happens, and this reaction results in an electrical signal output, normally a current output. This current can be used to infer important data from the analyte such as concentrations. As the name implies, electrochemical sensors are based on the principle of electrochemistry. Electrochemistry is the study of chemical processes that cause electrons to move and generate electricity. These movement of electrons can be described by a reaction called redox reaction, which stands for reduction and oxidation. In electrochemical sensors, this reaction happens at the electrode surface. There are many electrochemical methods, and each method has a different electrical signal output. The methods are as follows[22]:

- Potentiometry: measures potential difference in volts
- Conductometry: measures resistance in ohms
- Amperometry or voltammetry: measures current in amps as a function of applied potential
- Coulometry: measures current as a function of time
- Capacitance: measures potential load in farads.

According to Simoes et al (citation above), electrochemical methods can be divided into two groups: interfacial methods and non-interfacial methods. Interfacial methods respond directly to the presence of an analyte on the electrode surface. This analyte presence results in an electrical signal disturbance which is measured. Some interfacial methods include potentiometry, voltammetry, and amperometry. Non-interfacial methods measure the electrical properties of the solution as a whole. Conductometry is a typical non-interfacial method because it measures the resistance of a solution using two electrodes that are equally spaced. Most of these electrochemical sensors are carried out in an electrochemical cell. An electrochemical cell consists of a working electrode (the electrode where the analyte is sensed), the analyte, and a set of complimentary electrodes used. These other electrodes are commonly referred to as reference electrode and counter electrode. A reference electrode is an electrode with a known, constant potential. An ideal reference electrode should be insensitive to the composition of the solution being

studied[22]. Some examples of widely used reference electrodes include Normal Hydrogen Electrode (NHE), Standard Hydrogen Electrode (SHE), saturated calomel electrode (SCE) and saturated silver/silver chloride electrode (Ag/AgCl). The counter electrode establishes a connection to the electrolytic solution so that current can be applied to the working electrode, hence, they should be conductive but also stable. Some widely used counter electrode materials include platinum, gold, and carbon[2]. In addition to these electrodes, electrochemical sensing requires the use of a potentiostat which maintains the cell at a constant potential or monitors the electric current of the electrochemical system at a constant or varied potential, as in the cases of amperometry or voltammetry respectively. Figure 1-4 illustrates an ideal electrochemical cell with three electrodes[22].

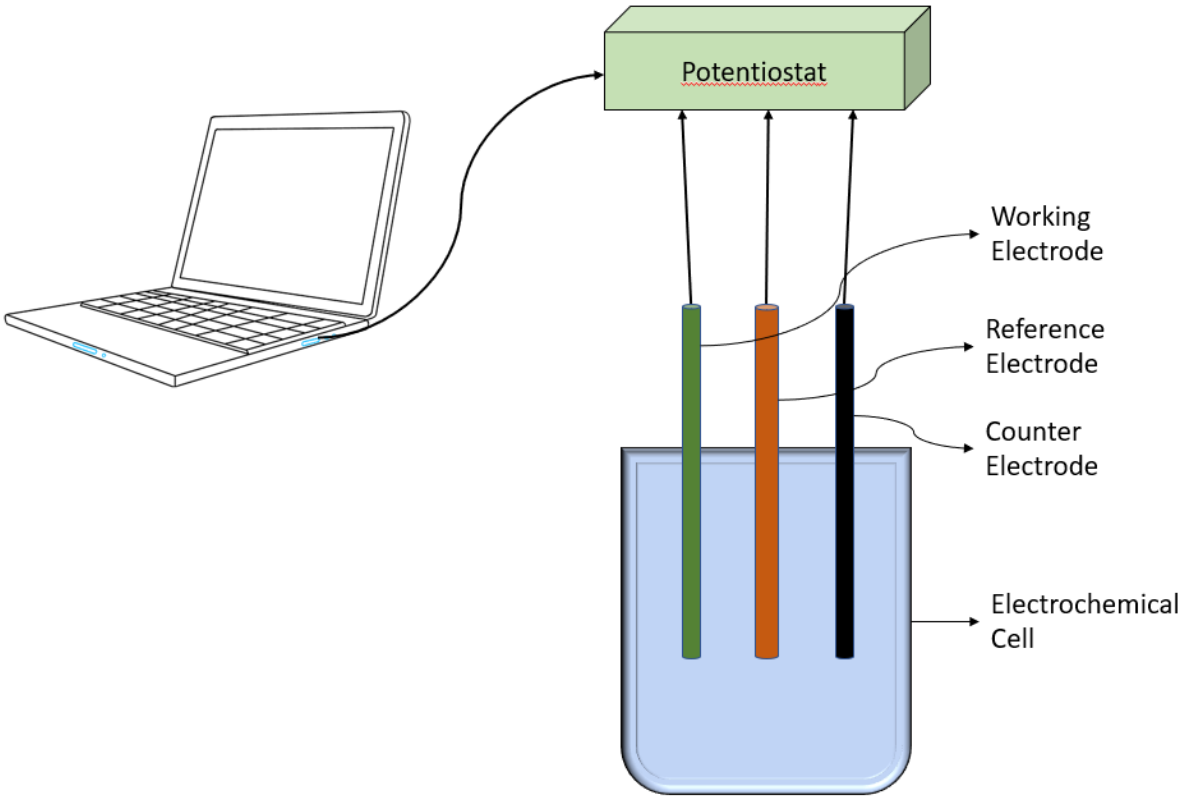

Figure 0-4: Conventional three-electrode electrochemical cell setup

Potentiometry, which is an interfacial method measures the accumulation of a charge potential at the working electrode compared to the reference electrode in an electrochemical cell. It provides information about the ion activity in an electrochemical reaction. A notable example of potentiometry is a pH meter, which has a glass membrane electrode and a reference electrode. The meter produces a potential difference of the solution on both sides of the membrane and converts it to a pH value. Amperometry is the electrochemical method of measuring the current flowing through a working electrode as a constant potential is passed to the working electrode. Oxidation or reduction occurs at the surface of the working electrode, and the measured current correlates to the amount of oxidized or reduced species on the surface. Figure 1-5 shows a typical amperometry measurement[23].

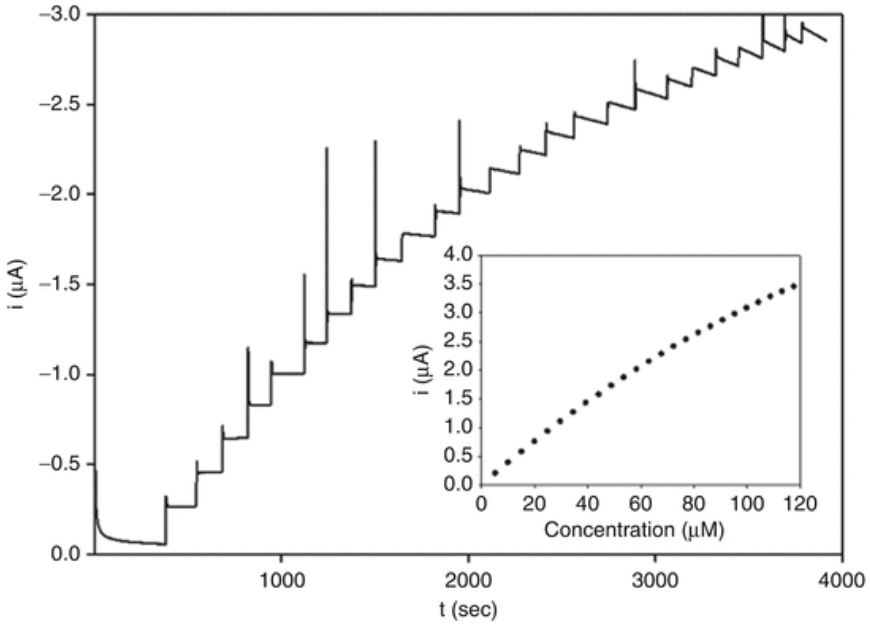

Figure 0-5: A typical chronoamperometry experiment showing current-time response of an immobilized enzyme.

The method of voltammetry is also like amperometry with the application of a potential but in its case, a varied potential is applied between the electrodes and the resulting change in current flow is measured. The varied potential that is applied to the electrode surface leads to oxidation or reduction of electroactive species in the solution hence, different species or analytes can eb sensed based on their oxidative or reductive properties. The different types of voltammetry are linear, pulse, and cyclic sweep or cyclic voltammetry. This biosensing project was carried out using electrochemical sensing, and more specifically using the interfacial methods of cyclic and pulse voltammetry, which fall under the voltammetry category described above. In cyclic voltammetry, the potential is swept in the positive or negative direction, starting from a set initial potential value, and ending at a final potential value, at a set sweeping speed with units of mV/s. The potential keeps sweeping back and forth until the number of desired cycles are met. Cyclic voltammetry has a link between its scan rate and the current measured and this link tends to affect its sensitivity hence, it is more generally used for exploratory purposes. Pulse voltammetry on the other hand doesn't have a sweep/scan rate parameter and is better suited for quantitative determinations of analytes. A resulting voltammetry plot is called a voltammogram, and the measurements are plotted as current vs voltage.[2] These two methods are used in this project in sensing dopamine, and they are compared to each other. More discussion on this sensing topic is presented in Chapter 4

Electrochemical sensing has many advantages and benefits as it has disadvantages. To compare it to other biosensing transduction methods however, some of the other sensing methods will be briefly defined. Optical biosensors are the most common class of biosensors, with a popular example being the glucose sensor for diabetics. Optical detection utilizes the interaction between an optical field and a biorecognition element. Biorecognition elements used in optical biosensors include but are not limited to enzymes, antibodies, nucleic acid, receptors, whole cells, and whole tissues. Some optical biosensing techniques include Surface Plasmon Resonance (SPR), fluorescence, evanescent wave, optical waveguide interferometry, colorimetry. SPR, evanescent wave, and fluorescence use the evanescent field close to the biosensor surface and detect the interaction between the biorecognition element and the analyte[24].

Optical biosensors emit an optical signal which is directly proportional to the concentration of the analyte. They can also be classified into two groups: label-based or label-free manner. The label-free manner involves interaction of the analyte with the transducer for signal detection while the label-based labels the analyte with fluorescent tags such as dyes, and the optical signal is generated by a colorimetric, fluorescent or luminescent method[25]. Optical biosensors are said to offer fast detection, high sensitivity, real-time monitoring as some advantages[26]. They don't require a reference sensor, as the comparative signal can be generated using the same source of light and the sampling sensor, unlike in electrochemical sensing. Fiber Optic based sensors (FOBS) are another example of optical biosensing. These FOBS rely on optical transducers that convert light signal to electrical signal to be displayed on a display. In FOBS, a light signal propagates down the optical fiber, interacts with the biorecognition element, and is sent back to the detector for deciphering. An advantage of FOBS is that they are electrically safe and small enough to reach small areas of the body[27]. Another major advantage is that they are immune to electromagnetic interference. This helps with clean and accurate sensing signal results.

Thermometric biosensors are formed on the basis of biological reactions that produce heat[28]. The reaction takes place in a small enzyme packed bed reactor. A substrate enters the bed and gets converted to a product. During this process, heat is produced and the difference in temperature between the substrate and the product is measured by thermistors. Currently, thermometric biosensors are used for estimating serum cholesterol. Cholesterol gets oxidized by the enzyme cholesterol oxidase and heat is generated which can be measured. The application of thermometric sensors however is limited because not all biological reactions in the body produce heat. Hence, electrochemical sensors can already be seen as superior to thermometric sensors[29].

Piezoelectric biosensors are based on the principle of sound vibrations and are also called acoustic biosensors. Piezoelectric biosensors have crystals, which are the sensor part of the sensors. They work on the principle of oscillations changing due to a mass bound on the crystals surface. Alternating voltage given to the surface of a piezoelectric material causes mechanical stress or oscillations. This alternating voltage when applied to this biosensor cause mechanical oscillations of the crystal and the frequency of oscillation is measured. If an analyte is bound to the crystals surface, the oscillation frequency changes and this change in frequency is proportional to the mass that is bound to the surface of the crystal[30]. This is how analytes are detected. Piezoelectric biosensors succeed in label free determination of analytes as they don't have to be modified with any type of markers as in some optical biosensors. As seen from cited papers however, this biosensor is limited in its ability to determine substances in solution because the crystals may cease to operate in viscous liquid.

All methods of biosensing that have been developed or are currently being researched have their advantages as well as their disadvantages. However, since this report is about fiber based electrochemical sensors, here are some of the reasons why this method of sensing was chosen over the others: electrochemical biosensors do not suffer the drawback of high sensor setup complexity and cost. For in vitro sensing, the equipment needed for sensing setup are the electrodes mentioned above and a potentiostat which is widely available. Also, for electrochemical sensing, to achieve better sensing results, different working electrode materials are explored, and most times, the working electrode is modified using electrochemical methods which are relatively cheap and do not require additional equipment. When compared to Surface Plasmon Resonance(SPR) which is an optical biosensing method, electrochemical sensing shows promise for an easier and cost-friendly setup, as current commercialized SPR instruments are expensive and bulky[24]. This limits the extent of their application. Another advantage of an electrochemical sensing system is easy miniaturization and use with small analyte volume. Although a standard electrochemical cell contains three electrodes, most cells can be shrunk to two-electrode systems

for easy in-vivo sensing. The idea of this project using optical fibers improves the chances for miniaturization of an electrochemical cell with its working electrode as a fiber electrode, whose diameters extend down into the nanometer range.

1.2 Motivation for biosensing work

Reviewing the advantages listed above led to the motivation for using an electrochemical method of sensing and using optical fibers as the sensing element. Optical fibers have various properties which lend to them being good biosensing candidates. More on optical fibers and their fabrication and properties is discussed in Chapter 2. One property is them being immune to electromagnetic interference. This property aids in preventing unwanted noise from nearby electrical sources and making them electrically safe for in-vivo applications. Optical fibers also tend to be thin as mentioned previously and would be able to reach hard-to-reach areas of the body. In particular, this project focused on dopamine sensing, which would mean sensing in the brain. The brain is known to be a very complex human part and also having areas notoriously known for being hard to reach. Using an optical fiber could help in reaching areas of the brain that otherwise could not be accessed. Another motivating factor for this project was the prospect of having flexible and wearable biosensors. Optical fibers are thin and can be woven into textiles. With sensing capabilities embedded, a wearable and breathable sensor can be created from a woven or knitted optical fiber design. This would lead to a comfortable point-of-care sensor, and also increase the user or patient experience.

1.3 Existing electrochemical based sensing technologies

There are numerous biosensing technologies that are in use in the real world, and more technologies that are still in testing and development phase. A common everyday example would be a pregnancy test stick. A pregnancy test is a biosensor and operates on an optical biosensing principle. Another example is a Fitbit watch or patch that monitors heart health, oxygen levels in the body and so on. These sensing technologies are not invasive and are used outside the body. To give a little more background to the work done in this report, some existing and developing biosensing technologies, specifically electrochemical based, will be discussed. This will help put my work on electrochemical sensing in perspective of real-world applications and help in visualization of a fully realized dopamine biosensor.

Iguchi et al developed a flexible and wearable amperometoric biosensor for tear glucose measurement[31]. The flexible sensing platform was based on electrochemical sensing methods, and used a two-electrode system. The sensor was constructed by immobilizing glucose oxidase (GOD) on a flexible film-like oxygen electrode. This oxygen electrode was fabricated using soft MEMS (Micro Electro Mechanical Systems) technique. The developed film-type oxygen electrode has four layers: a flexible gas-permeable membrane made from polypropylene, a 200nm thick Pt electrode and an Ag/AgCl electrode, a membrane filter that contains the electrolytic solution (0.1mM of KCl), and a non-permeable membrane with thickness of 50um. No adhesives were used in the fabrication of the electrode. More on the fabrication process of the individual electrodes and the membrane layers is described in the article[31]. The electrode was constructed in a sandwich style configuration, with the membrane filter containing the electrolytic solution sandwiched between the gas-permeable membrane with the electrodes and the non-permeable membrane layer. This sensor sensed glucose by measuring the oxygen consumption induced by enzyme reaction of the enzyme immobilized membrane using the two-electrode electrochemical method. A constant potential of -0.55V vs Ag/AgCl was applied to the working electrode and the outputs were recorded by a potentiostat. From the experimental results, a relationship between the glucose concentration and the output current was confirmed in a range of 0.025-1.475mM/L, with a correlation coefficient of 0.998 which was gotten from regression analysis. More of the results in relation to pH and temperature are discussed in the cited paper. The paper also reported a 10-minute delay in

increase in tear glucose after blood glucose level increase. Apart from this delay, results were gotten without significant variation and stability. Because of the flexible nature of this developed sensor, continuous tear glucose monitoring could be carried out with sufficiently stable and sensitive results. If commercialized this would be a positive breakthrough to non-invasive continuous glucose monitoring research.

An emerging class of sensing technology specifically for sensing analytes in human sweat is the temporary tattoo style sensors. Although these are not fully operable yet, the push in their research shows that integrating this sensing method with potentiostatic control, wireless data transfer and energy harvesting will lead to a fully functional 'electronic skin' in coming years. 'Electrochemical sensing based on printable temporary transfer tattoos' is an article by Windmiller et al that presents an electrochemical biosensing method using temporary tattoos[32]. The aim of this group's research was to improve upon the concept of flexible screen-printed electrochemical sensors which don't stick too well to the skin which is their sensing organ. The electrode design is patterned onto a release agent-coated base paper using screen printing. An adhesive sheet with a protective coating is then applied to the printed electrochemical sensor. In the case of physiological sensing, the base paper is removed and the tattoo pattern is applied to the skin. The electrochemical sensors are then integrated with a handheld 3-electrode potentiostat via pressure contact with a medical-grade adhesive. A micropotentiostat can also be mated with the electrode via an adhesive patch and the total system could be worn on the skin for a long time period. The working electrode material is carbon fiber (CF), and some CF segments were dispersed within the tattoo ink. The CF dispersed provides mechanical reinforcement for the sensor, and this resiliency was tested by stretching of the skin, twisting, and pinching[32]. Cyclic voltammetry was also carried out to test the difference between sensing signal from CF-reinforced sensor and the unreinforced sensor. The CV results showed increased sensing current for the CF-reinforced sensor. More in depth discussion on the results form testing can be found in the cited paper. Further work on this idea will involve functionalization of the tattoo sensor's electrodes with enzymes for higher recognition and improved selectivity towards target analytes.

Another sensing technology that is showing a lot of promise is wireless biosensors, and research in this area has grown rapidly over the past two decades. Wireless biosensors are hybrid devices that collect bio data from their local environment, and then process and transmit the analytical information to a remote device by wireless technology[33]. Wireless sensors also have found use in point-of-care diagnostics such as pregnancy testing, diabetes management, and other physiological monitoring. Point-of-care devices improve the quality of life of patients as it allows for monitoring of health symptoms from the comfort one's home. Electrochemical sensors are prevalent in the wireless chemical sensor field with potentiometry and amperometry being the dominating sensing methods, and the paper by Koehne et al. shows an example of this. The paper describes a carbon nanofiber electrode array for electrochemical detection of dopamine[34]. In the described project, a carbon nanofiber (CNF) electrode array is integrated with a Wireless Instantaneous Neurotransmitter Concentration Sensor System (WINCS). This project is a good example of an existing technology to review in regard to the content of the project in this report because this report is based on electrochemical biosensing of dopamine using fibers.
Carbon Nanotubes and CNFs have shown promise as neurochemical recording electrodes due to their high sensitivity, rapid electron transfer kinetics, and biocompatibility. The CNF array detects dopamine using fast scan cyclic voltammetry (FSCV) in a two-electrode electrochemical system. The CNF nanoelectrode array was prepared on a silicon wafer using vertically aligned CNFs 100um in diameter. The reference electrodes used in this experiment are Ag/AgCl electrodes. Details on the construction of the working fiber electrodes and the reference electrodes are discussed in the cited paper[34]. The wireless part of this proposed sensor, the WINCS, incorporates both the FSCV and digital telemetry to display the electrochemical measurements on a PC in real time. The hardware components (which consist

of analog circuitry for FSCV, a Bluetooth transceiver, and a microcontroller) of the WINCS are printed on a printed circuit board (PCB). The FSCV for dopamine sensing was carried out over the electrode range -0.4V to 1.0V at a scan rate of 300V/s. The resulting sensing currents showed correlation between dopamine concentrations and recorded current value. A major advantage of the CNF platform is detection of neurochemical analytes over a large area because of the multiple sensing electrode tips present in its array, but still with high spatial resolution. The cited paper also compares the results of dopamine detection using a single Carbon Fiber Microelectrode (CFM) and the CNF platform, and found that their sensing capabilities are comparable.

A similar wireless sensing technology using voltammetry is described in the paper by Jung et al[35]. The paper presented a disposable cyclic voltammetry (CV) tag that is printed on a plastic film and integrates wireless power transmitter, electrochemical cell and signage through a gravure printing method. The CV tag detects the presence of solutes in a solution dropped on it using a two-electrode printed electrochemical cell, and it displays the solutes on the signage of the tag in about five seconds. Since there is no technology advanced enough to build a wireless and cost-effective disposable CV system, the project explores the premise of wireless transmission by studying the basics of wireless power transmission technology of RF devices. The details on how the power circuit for the tag was produced and how a wireless waveform that scans the electrochemical cell to stimulate redox reaction was generated are discussed in the cited paper[35].

The technologies and research work described above are summarized in Table 1-1, along with other applications of electrochemical methods in biosensing. The table shows the usefulness and advantages of electrochemical sensing and helps the reader put the biosensing work described in this thesis in perspective of practical applications.

Table 0-1: Summary of Electrochemical biosensing technologies

Electrochemical Method	**Target Analyte**	**Working Electrode**	**Device form/given name (if provided)**	**Pros/sensitivity**	**Reference**
Cyclic Voltammetry	sweat	SWCNT	Flexible tag	Wireless electrochemical sensor	[21]
Fast scan Cyclic Voltammetry	Dopamine	Carbon Nano-Fiber		High sensitivity due to CNT and CNF use, wireless data transmission	[34]
Cyclic Voltammetry	Sweat	Carbon Fiber	Electronic skin/temporary tattoo	This sensor is compatible with the irregularities of the human skin surface	[32]
Amperometry	Tears (specifically glucose)	Platinum		Flexible sensor for continuous tear glucose measurement	[31]
Cyclic Voltammetry	Cancer biomarker(a-fetoprotein)	Graphene sheets		Employs dual signal-amplification for greater sensitivity.	[36]

				Detection limit: 0.02ng/mL^{-1}	
Potentiometry	pH	pH electrode	Wireless sensor tag	Has autonomous sensing capabilities compatible with IoT and a portable size	[37]
Amperometry	Saliva (glucose)	platinum	Mouthguard biosensor	Sensor has continuous wireless glucose measurement function	[38]
Amperometry	Alcohol oxidase	Prussian Blue conductive carbon	Flexible tattoo-based alcohol sensor	Developed sensor shows promise for real-time detection of alcohol levels and wireless data collection	[39]

2 CHAPTER 2- Fiber Fabrication

Biosensing using electrode-embedded optical fibers shows a lot of promise for biosensor device miniaturization and less invasive sensing. Having optical fibers fabricated specifically for a sensing application can improve the sensitivity of that fiber. This chapter discusses the basic structure of optical fibers, how they are drawn, how electrodes are embedded in these fibers, and how the optical fibers used in this thesis's work were fabricated.

2.1 Optical Fibers

Fiber optics refers to the transmission of light through very fine glass or plastic fibers. Optical fibers are made from glass or plastic, roughly have the diameter of a human hair, and can be drawn to be miles long. Silica-based fibers are the waveguides of our present and the foreseeable future. They currently have prominent applications in international and domestic telecommunications. Most homes are already fitted with optical fibers providing telephone, internet and multiple channel high definition television services[40]. Recognizable properties of fibers are their small size, light weight, and dielectric property that protects them from emitting and being affected by electromagnetic radiation. Optical fibers consist of three basic elements which are the core, the cladding, and the outer coating, as shown in typical optical fiber setup shown in Figure 2-1[41]. The core and cladding are usually either made from plastic or glass, with one having a slightly lower refractive index than the other and in most cases, cladding is the component with the lower refractive index[42].

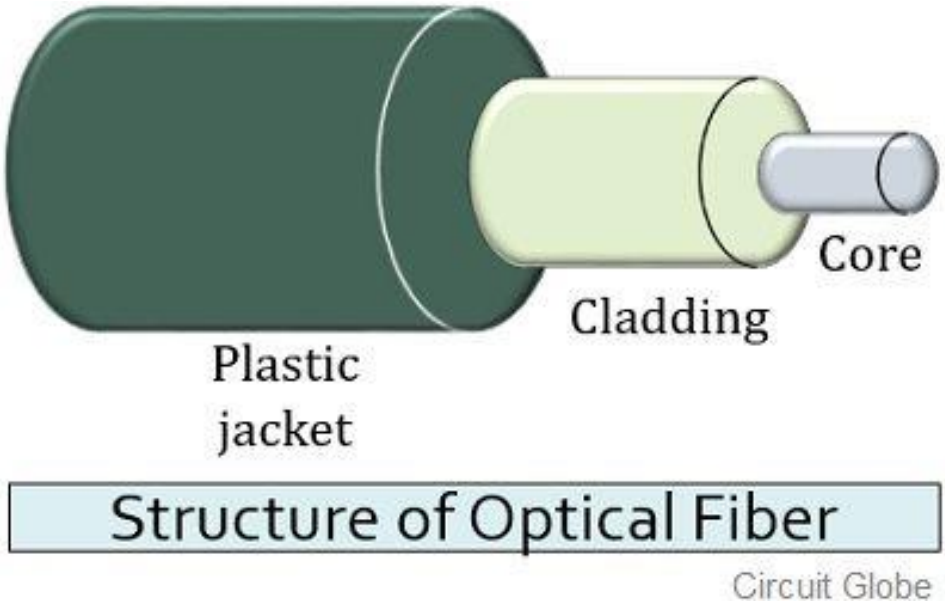

Figure 2-1: Structure of Optical Fiber (Ref: https://circuitglobe.com/difference-between-optical-fiber-and-coaxial-cable.html)

Light is transmitted along the core of these fibers by a phenomenon called Total Internal Reflection or TIR, pictorially described in Figure 2-2. This phenomenon guides the light rays in along the fiber by keeping them confined in the core and allowing no ray refraction. TIR which is a special refraction case is described by Snell's law defined as:

$$n_I \sin I = n_R \sin R$$

Where n_I and n_R are the refraction indices of the cladding and core material that the light is passing through, and I and R represent the angle of incidence and angle of refraction respectively of the beam of light[42].

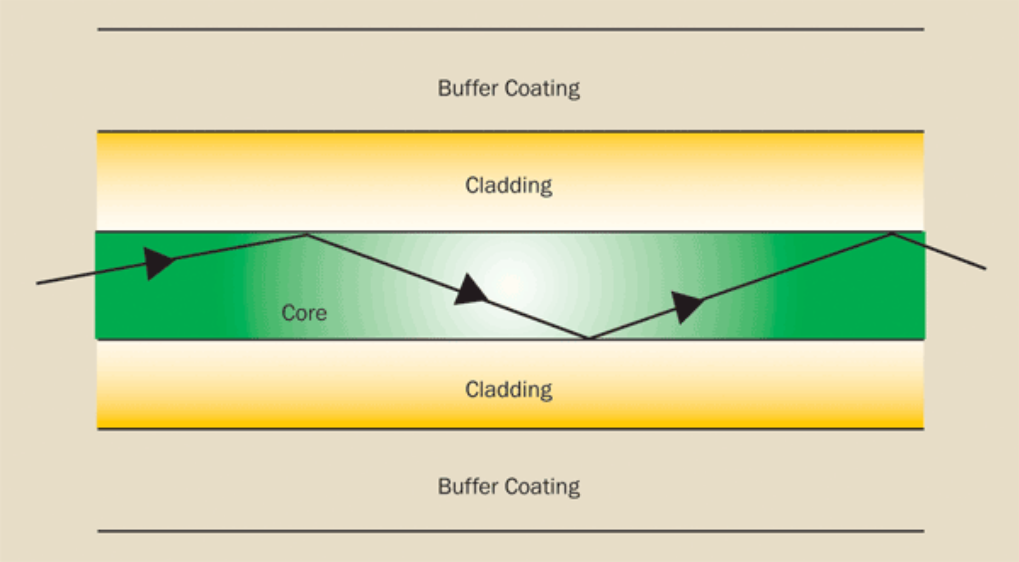

Figure 2-2: Core, Cladding, and outer coating of an optical fiber (source: https://www.photonics.com/Articles/Fiber_Optics_Understanding_the_Basics/a25151)

There are three basic types of optical fibers: single-mode, multimode step-index, and multimode graded index fibers. For a single mode fiber, the light beam travels straight through the fiber and there are no reflections from the core-cladding boundaries. In multimode fibers, the core is wider and allows more light through, leading to beams reflecting and bouncing off the core-cladding boundary. The refractive index in the core also changes in a step-like fashion, contributing to the different modes travelling through the core. The main difference between the multimode step-index and multimode graded index is the manner in which the refractive index changes in the core. Graded-index fibers have an index of refraction that changes gradually while the other has a step-like index change. Optical fibers are normally characterized by their core diameter, core and cladding indices of refraction, numerical aperture (measures angle at which light rays enter the fiber), modes, and bandwidth.

All these properties lend to the sensing capabilities of fibers as optical fiber sensors (OFS). In OFS, light is normally propagated down a fiber to the analyte to be sensed and reflected back to a detector. The analyte is sensed by analyzing the transmitted light and the reflected light, looking at their property changes. Various ideas and methods regarding fiber-optic sensing have been proposed for various measurands and applications, but not all these ideas have been commercialized. Optical fiber sensors have unique advantages such as EMI immunity, small size, light weight, high sensitivity to name a few and these lend to them being good sensing platforms. Measurands that have been explored with OFS include pressure, acoustic, temperature, strain, current/voltage, vibration, bending, displacement, and bio analytes[43]. In this thesis's work however, the optical fibers are modified with electrodes, giving rise to multimaterial fibers. This fiber type enables other biosensing methods, such as electrochemical sensing, to be realized. This method of modifying the fibers will be explained to better understand the project.

2.2 Multimaterial Fiber Fabrication

Electronics are evolving from rigid, bulky structures to more flexible and pliable structures after major research and breakthroughs in the fields of materials, mechanics and some specific device properties. This

makes them easier to integrate into our everyday lives. The method used for the fabrication of the fibers used in this thesis is synthesizing electrodes within thermally drawn fibers. Thermal drawing, is a typical approach for producing optical fibers in the industry. Hundreds of kilometers of optical fibers are produced by heating a macrostructured preform in a fiber draw tower[44]. The preform is fed into a furnace, the furnace softens the material, and a force (gravity or external) pulls the molten blob at the preform tip and stretches it into a thin strand. The strands diameter is monitored by a gauge to ensure consistency in size throughout the fiber[45]. Figure 2-3 pictorially depicts the fiber drawing process[46].

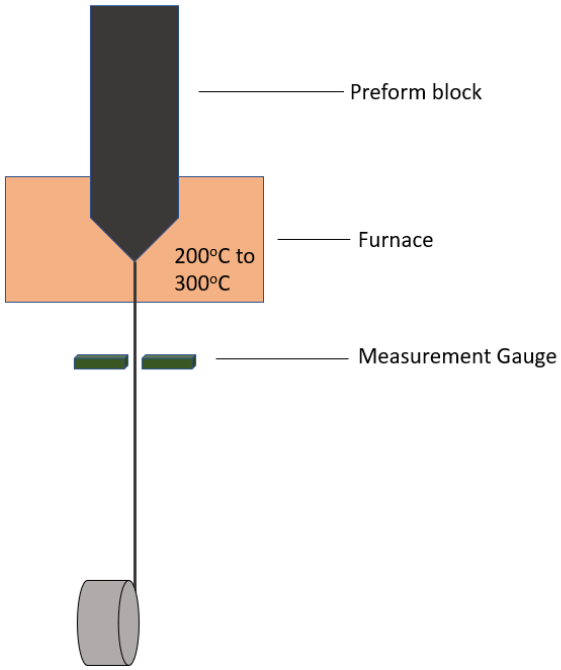

Figure 2-3: Fiber thermal drawing tower schematic

The size of the fiber is controlled by the drawing temperature of the hottest part of the furnace, the feed-in speed of the preform, and the pull on the fiber[47]. This fabrication process is used for the many miles of optical fibers used in communications networks across the globe. Over the years, thermally drawn fibers have evolved from simple translational symmetry, where the fiber material and geometry are similar to that of its preform, to complex fibers that are co-drawn with different materials and geometries. This area of multimaterial fibers has led to the emergence of fibers with sophisticated structures and functionalities. The introduction of different materials however into thermal drawing increases the complexity of the thermal drawing procedure and imposes constraints on the material combinations that are compatible with this drawing approach. Materials have to be chosen whose boiling points are below that of the drawing furnace. The outer cladding or backbone of the fiber should be amorphous so as to resist crystallization during the drawing[45].

There are various methods of multimaterial preform fabrication. The four general classes are rod-in-tube approach[48], extrusion[49], stack and draw approach[50], and thin-film rolling approach. The rod-in-tube approach relies on inserting a rod of one material into a tube of another material. This insertion creates a preform with a core-cladding structure. This method allows for a wide range of materials to be inserted into the preforms core, with an interesting example being a powder[45]. Extrusion is a process where a soft material is pushed through a die under pressure to create a fixed cross-sectional profile. The material that is pushed down is called a billet, and this billet is heated to the softening temperatures of its

component materials. To create a multimaterial fiber, the bidet consists of vertically stacked disks of the materials of interest[49]. In the stack-and-draw method, rods or tubes from single or multiple materials are assembled into a preform and sealed. The dimensions of the rods are determined by the dimension of the target fiber. Rods can be stacked in other hollow rods and so on to achieve the required fiber dimension and to attain complex fiber structures. This approach has been extensively used in making preforms for micro-constructed fibers[45]. The fourth general class is thin-film rolling. In this unique process of introducing polymers in preforms, a thin polymer film is rolled and then thermally consolidated under vacuum. The consolidation continues until the individual films in the polymer fuse. The rolling can be performed multiple times to realize a more complex cross-section[51]. A void can also be introduced into the post-consolidated structure such that the void is filled with a conductor material, the structure is rolled again in additional thin films and then reconsolidated. These preform fabrication methods described above are the basis for many electronic and photonic thermally drawn multi-material fiber devices.

In addition to the thermal drawing method of fabricating multi-material fibers, there are some post-thermal drawing fabrication methods that are described in the paper by Yan et al.[52]. The first technique is the injection of materials into the capillaries of already thermally drawn fibers. It is more formally known as pressure-assisted melt filling technique. This technique is used to create metallic nanowires in hollow channels in microconstructed silica fibers in the work by Lee et al.[53]. A gold wire is inserted into the capillary of a silica fiber with inner and outer diameter 80um and 200um respectively. The capillary was then spliced with a silica Photonic Crystal Fiber (PCF) and placed in a furnace to hear up to the melting temperature of gold. After heating, argon gas pressure was applied at the other end of the capillary until the gold completely filled the hollow channel of the PCF. A prerequisite of this technique is that the materials being injected needs to have a melting temperature significantly lower than the softening temperature of silica[54]. Figure 2-4 shows a spliced-fiber pressure filling technique[53].

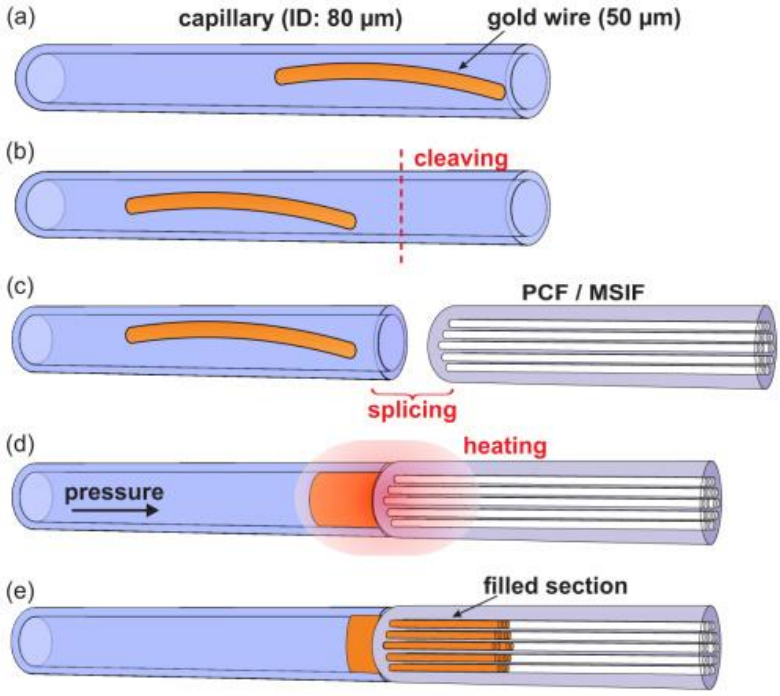

Figure 2-4: Pressure Assisted Melt-Filling Technique. Image (Source: https://www-osapublishing-org.ezproxy.lib.vt.edu/oe/fulltext.cfm?uri=oe-19-13-12180&id=217393)

Another method under post thermal drawing fabrications to create a functional multimaterial fiber is functionalization of small portions of constructed optical fibers, such as the tips or part of the fiber cladding. Several methods that have been developed for this include patterning directly onto the tip of optical fibers, transferring metallic or dielectric structures that are locally fabricated onto the optical fibers as seen in Figure 2-5 [55], and direct deposition of target functional materials on the fiber. The micro fabrication techniques involved in patterning include photolithography, nanoimprinting, interference lithography, electron-beam lithography, focused ion-beam milling, two-photon polymerization, and femtosecond laser ablation[56]. Zhang et al. gives an in depth review on functionalizing Molybdenum Trioxides nanoflakes onto an optical fiber biosensing platform for detection of bovine serum albumin[57]. Yu et al. also provides a comprehensive review on patterning metasurfaces on optical fibers and discusses its applications. They give a review on various methods of metasurface fabrications and patterning[58].

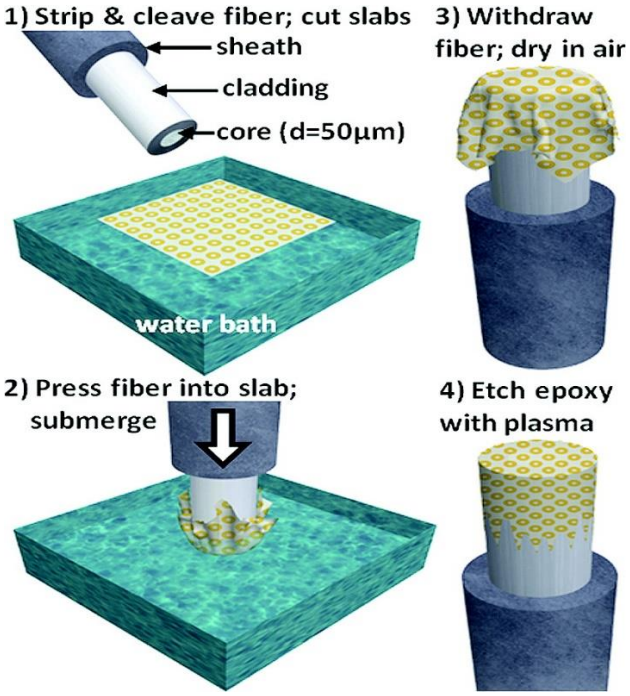

Figure 2-5: Procedure used in fabricating and transferring an array of metastructures on an optical fiber facet. (Source: https://pubs-acs-org.ezproxy.lib.vt.edu/doi/10.1021/nl103730g)

2.3 Multimaterial Fiber Functionalities

There has been a significant advance in the fabrication and application of thermally drawn multi-material fibers. A single fiber can be embedded with several materials and functionalities, enabling its use in the development of compact devices with multiple applications. We will discuss some achieved fiber architectures and functionalities.

Electronic Fibers: Electronic functionalities in drawn fibers can be divided into three categories that depend on the conductivity of the embedded electronic material[52]. They include metals or polymers with high conductivity (normally used as electrodes or resistors), semiconducting materials with the ability to control their current density via a field effect, and insulating materials which are used for their dielectric capabilities. A popularly explored application of fibers with integrated electrodes(first category) is neural probes in bioengineering[52]. Canales et al. demonstrates the use of multifunctional fibers for simultaneous optical, electrical, and chemical interrogation of neural circuits in vivo[59]. The paper presents a polymer-based fiber probe for simultaneous optical stimulation, neural recording, and drug

delivery with high resolution. The experiment was carried out in free moving mice, and the choice of polymers used in the thermal drawing allowed for production of a flexible device that maintained its functionality during bending. The multielectrode probes used in this study were thermally drawn with polyetherimide (PEI) and polyphenylsulfone (PPSU) as the cladding material, and tin as the electrode material. Detailed fabrication steps are described in the cited paper[59]. The dielectric properties in some thermally drawn electronic fibers have been exploited and the resulting devices pave the way for applications in distributed pressure sensing, acoustic sensing and positioning, flow measurement, etc. [60]. A promising dielectric material is poly(vinylidene fluoride) (PVDF) because of its high dielectric constant. Lestoquoy et al. [61] demonstrate a fiber capacitor which exhibits low-loss capacitive behavior of up to 20kHz. The design is realized by sandwiching PVDF thin film between Carbon Paste Electrodes (CPE). Integrating an array of capacitive fibers into a woven textile can generate a touchpad sensor that doesn't exhibit inter-channel crosstalk. Finally for electronic fibers, semiconductor-based electronic fibers have been exploited, with applications in temperature sensing[62]. Integrating thermally-sensitive semiconductors whose conductivity varies with small changes in temperature makes these fibers candidates for high spatial resolution heat sensing[52]. Electronic fibers are excellent for various sensing operations, and more specifically, are the type of fibers used in the sensing work presented in this thesis. Electronic fibers with embedded conducting electrodes are used as the working electrode component of the electrochemical cell used in sensing dopamine. More on their specific sensing application is presented in Chapter 4.

Optoelectronic Fibers: Interfacing metallic electrodes with semiconducting domains opens the door for optoelectronic functionalities. Optoelectronic fibers combine the optical properties of the fibers with the electronic properties of the embedded electrode. The semiconductors used in optoelectronic fibers are made of chalcogenic glasses, which are glasses formed based on the chalcogen elements(oxygen, sulfur, selenium, tellurium)[63]. The glasses exhibit special properties such as a large refractive index, range of transparency in the infrared region, phase change attributes[52]. The first metal semiconductor insulator optoelectronic fiber was fabricated by thermal drawing in 2004 by Fink et al. The fiber comprised of an amorphous semiconductor core contacted by metallic nanowires, and surrounded by a cylindrical shell resonant optical cavity[64]. The core of the fiber produces current when the fiber is struck with light hence, the tunable fiber was used as a photodetector, and is sensitive to incoming light along its entire length. To test the optoelectronic properties of this fiber, the paper describes a process of simultaneously measuring the electrical photocurrent and the optical reflectivity while externally illuminating the fiber. At the resonant wavelength (the wavelength of the illumination source that corresponds to the optical cavity resonance), the photocurrent value was enhanced and the back-reflection was diminished, showing that the light source reached the photo detecting core. Further advancements with this fiber technology involve creating a functional fabric by weaving the flexible fibers into a grid structure[64].

Multifunctional Fibers (distributed pressure and temperature sensing): To further demonstrate the functionalities of multimaterial fibers, we will review Yu et al. work that reports the fabrication of a thermally drawn fiber for distributed pressure sensing and temperature sensing[65]. Pressure and temperature sensing are of major importance in different industries. Pressure sensors are used in the medical field to accurately measure blood pressure[66], used in smart homes to ensure safe levels of various gases, and have various industrial applications to ensure worker safety and efficiency. Temperature sensors are widely used in personal and environmental sensing. In the present market, the more prevalent flexible pressure and temperature sensors platforms are often fabricated using thin-film technology[67]. However, using the polymer fiber pressure and temperature sensors described by Yu et al. would aid in the development of textile and wearable sensing applications as polymers are breathable and offer more flexibility. The fabricated fiber in the cited paper consists of thermoplastic materials,

thermoplastic elastomers, and metal electrodes all drawn in one fiber. The embedded electrodes act as a parallel wire transmission line in the fiber, and they are separated by a polymer material. The cited paper details the drawing methods, how the electrode is embedded and how the elastomers interact with the electrode to produce a sensing signal. Pressure was sensed with the fiber using a Vector Network Analyzer (VNA) to measure reflection signals resulting from an impedance drop along the fiber's length. The impedance drop correlates to applied pressure on the fiber. Temperature changes are detected by the polymer materials between the electrodes, and materials were chosen that are responsive to temperature. The test for temperature sensitivity involved heating sections of the fiber using a thermoelectric cooler and then measuring the reflection signal based on the temperature change using a VNA[68], like in pressure sensing application. As the fiber fabricated in this paper is said to show promise for textile/wearable sensing applications, the analysis presented includes weaving the fiber into a 2D grid structure and demonstrating its measurement capabilities. The results of this measurement is quantitatively and pictorially represented in the article[65].

This review of electronic and optoelectronic fibers and other multimaterial fiber applications points out the potential of integrating different complex functionalities in the confined space of a polymer or glass fiber. It also shows the importance of multimaterial fibers and increasing research on different material properties, architectures, and achievable fiber sizes will lead to increasingly complex and functional fibers.

2.4 Convergence Fiber Drawing

The sensing work demonstrated in this thesis is done using electronic fibers, which are optical fibers embedded with an electronic material e.g., electrodes. The specific fiber used for this work was fabricated using convergence drawing method. In convergence drawing, which is based on thermal drawing, metal wires are passed through channels inside a preform as seen in Figure 2-6. As the preform is heated by the furnace in three separate heat regions (top, middle, bottom) and drawn into a fiber, the channel size decreases and converges onto the metal wires. This method provides a way to embed high-melting temperature metal electrodes in the fiber while providing high conductive electrical connection. With convergence drawing, the temperature constraints on the material used as an electrode reduces leading to a wider application scope for multifunctional fibers. Tungsten(W) and copper (Cu) electrodes were used in the two separate fibers utilized in this work. Rein et al. [69] demonstrates this process by incorporating different electronic materials such as LEDs, photodetectors, and metal wires into a polycarbonate (PC) preform, producing hundreds of meters of fibers.

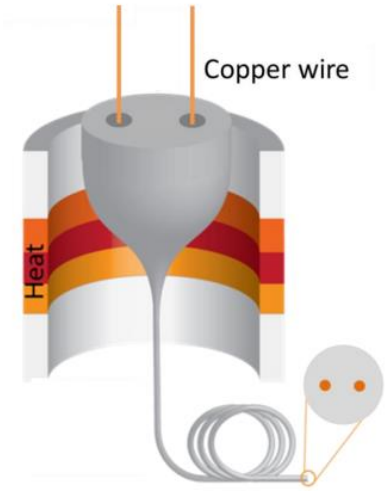

Figure 2-6: Convergence Drawing Method Setup

The multimaterial fiber used in the work described in Chapter 3 and 4 is fabricated by thermal drawing as discussed in the paper by Feng et al[70]. The paper describes the use of the fiber as a fiber-based triboelectric nanogenerator (FTENG) which is used as a wearable energy harvester. The fiber consists of a Polypropylene (PP) cladding and tungsten core. The 50um tungsten wire is fed into the 26mm diameter preform as it is being heated in the furnace and pulled down. A high draw-down-ratio during the drawing process is essential for the PP layer to be attached to the tungsten wire. During the drawing process, the PP cladding was also wrapped in an acrylic layer to produce the preform[70]. This choice was made because PP drops to low-viscosity when heated, and materials in a low-viscosity state easily flow when stress is applied, leading to breakage in the drawn fiber. Hence, the acrylic which is an amorphous material and presents stable diameters during draw procedures is used to contain the semi-crystalline PP cladding[71, p.]. The custom-built fiber draw tower used to draw the preform had temperatures of 145^{o}C, 245^{o}C, and 100^{o}C for the top, middle, and bottom respectively. The cross-sectional image of the fabricated fiber and the drawn fiber is shown in Fig 2-7 a and b respectively.

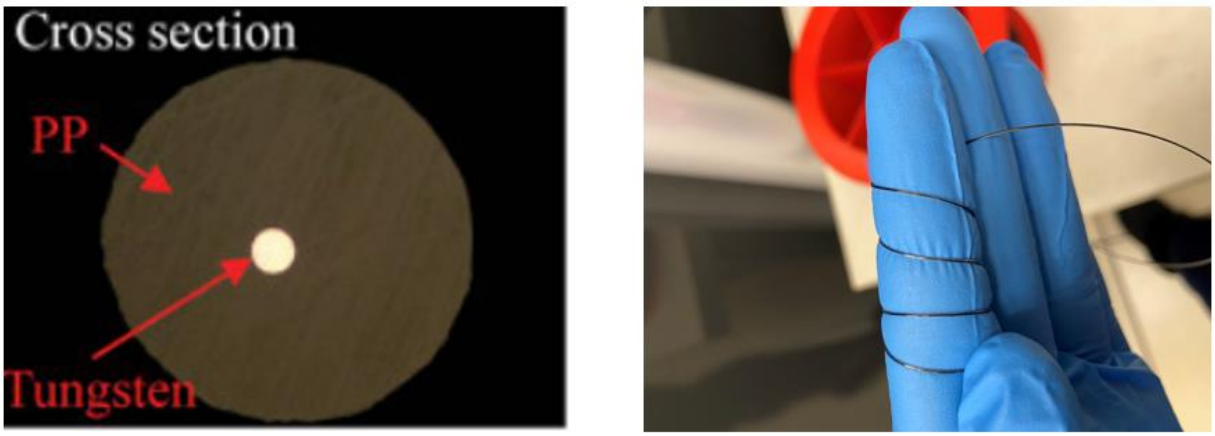

Figure 2-7: (a)Microscope image of the cross-section of the PP/Tungsten fiber, tungsten wire diameter:50um (b)flexible fiber wrapped around a finger

The other fiber used in this thesis' work is a Polycarbonate (PC) fiber containing a copper electrode. The copper electrode wasn't used in this work; instead, the electrode was taken out of the fiber and replaced with the other pure platinum wires that were used in the dopamine sensing results presented in Chapter 4. This fiber was drawn using the convergence fiber drawing method. The furnace drawing temperatures at the top, middle, and bottom of the furnace are 150°C, 285°C, and 120°C respectively. The diameter of the fiber is 800um and the diameter of the copper electrode is 125um. Fig 2-8c shows the microscopic image of the cross-section of the PC/Copper fiber. The figure shows the cleaved end of the fiber where the Pt wire was inserted for use in the electrochemical cell.

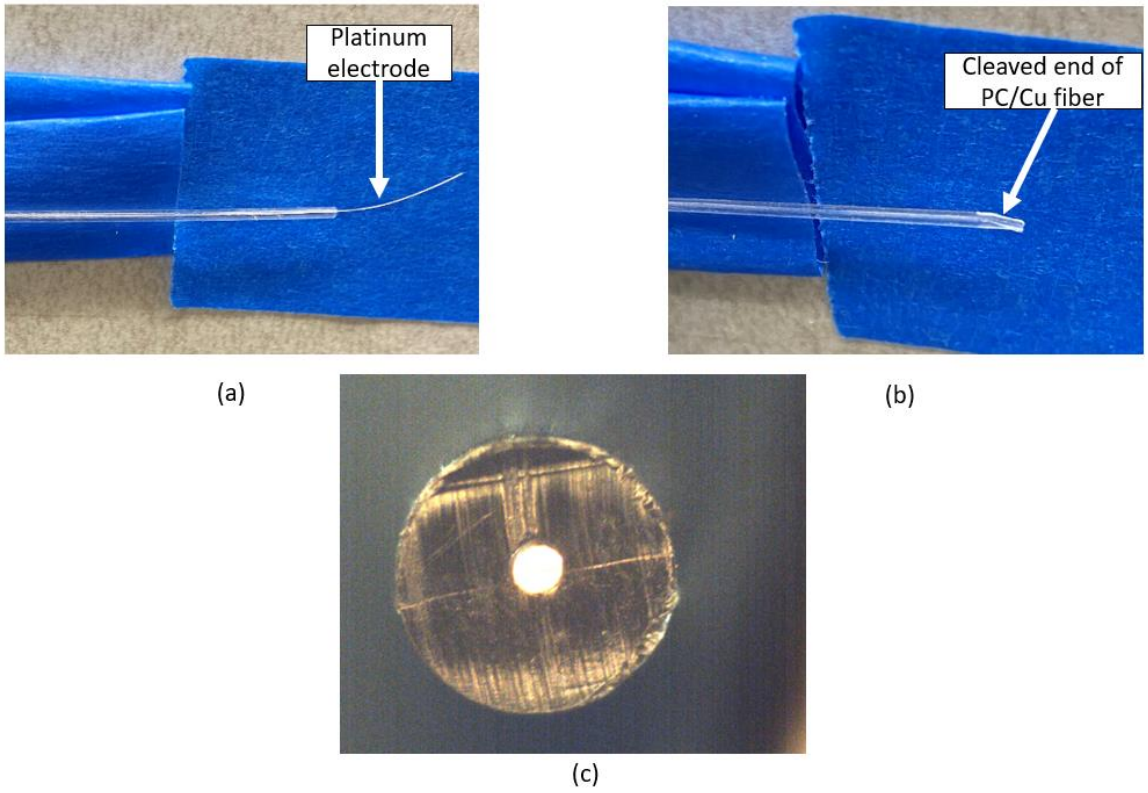

Figure 2-8: (a)PC/Cu fiber with copper electrode replaced by platinum wire (b)cleaved end of PC/Cu fiber (c)microscopic image of PC/Cu fiber cross-section

3 CHAPTER 3- Electrodeposition Procedure

The work we are focusing on in this thesis is the sensing of dopamine using fiber electrode. Since dopamine is neurotransmitter present in the brain, the electrode being used for sensing needs to be biocompatible. Hence, we are utilizing platinum as the sensing metal, which has been identified as a compatible metal for biological applications, among others[72]. The platinum however is not the base material of the electrode embedded in the fiber and is deposited using an electrodeposition method. This chapter will give a general introduction to the deposition procedures for metals, explain electrodeposition and why it was chosen as the deposition method, and describe the experimental procedure for the electrodeposition of platinum, including results and images characterizing the deposited electrode.

As described in Chapter 1, the different biosensing methods use different materials and techniques for sensing an analyte or bioreceptor. In electrochemical sensing, an electrochemical cell containing electrodes and an electrolytic solution is applied. In this sensing however, the working electrode if often tailored to the sensed analyte, i.e., the surface of the electrode is modified to increase sensitivity, selectivity, and biocompatibility. The most common working electrodes are noble metals, graphite, and modified forms of carbon or conducting polymers[73]. Noble metals can be defined as metallic elements that show resistance to chemical attack, even at high temperatures. They also show outstanding resistance to oxidation. The generally accepted list of noble metals includes ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, and gold[74]. We chose platinum as our working electrode material. From different studies, the most used working electrodes are platinum, gold carbon, and mercury. Amongst these however, platinum is said to be the favorite because of its electrochemical inertness and ease of adaptability in many forms[75]. Platinum however is more expensive than most metals because it is a much rarer naturally occurring metal[76]. Hence to make the developed biosensing platform more cost-efficient, we utilized deposition of the metal on another metal, in this case tungsten(W).

3.1 Basics of Deposition

Deposition is the act of applying film or layers of a material to the surface of another material. If this film is a thin-film, then the procedure is referred to as thin-film deposition. Although the term ‘thin’ is relative to the application, most procedures keep the film thickness to within hundreds of nanometers[77]. Deposition techniques fall into two broad categories, depending on the type of process. They are chemical and physical. In chemical deposition, a fluid solution undergoes chemical change at a solid surface, leaving a high-quality solid layer behind. Chemical process is often used in the semiconductor industry to produce thin films[78]. Some chemical deposition techniques include chemical bath deposition, spray technique, electroplating, electroless deposition, and chemical vapor deposition[79]. Physical deposition uses mechanical, electromechanical, or thermodynamic means to produce a solid thin film. Physical deposition can largely be divided into two groups: evaporation techniques and sputtering techniques[78]. Under these techniques are vacuum thermal evaporation, electron beam evaporation, laser beam evaporation, ion plating evaporation, direct sputtering, and radio frequency sputtering[79]. We will briefly describe some of these deposition techniques to give some insight and basis of comparison for the work described in this thesis. First up, under physical deposition is evaporation techniques. The general mechanism for these methods is changing the material phase from solid to vapor, and then converting back to solid phase on the substrate to be deposited. It also normally takes place under vacuum or controlled atmospheric condition. In electron beam evaporation(e-beam), an intensive beam of electrons vaporizes the target under vacuum environment[80]. E-beam evaporation can be used to deposit a wide variety of materials such as metals[81], oxides, and molecular materials. In laser beam evaporation also known as pulsed-laser deposition, a laser beam is used to gradually erode the material for depositing the thin-film in a vacuum chamber[82, p. 2]. Another popular physical deposition method is sputtering.

Sputtering involves bombarding a source material with ions, resulting in the ejection of atoms from its surface and condensation of the same ejected atoms on the substrate to be deposited. This process is carried out in a high vacuum environment, containing a metallic cathode and anode. The book by Piegari et al. describes in detail the sputtering process and it's different types[83]. The three processes described above are vacuum based techniques and have the advantage of depositing high quality thin films.

Under Chemical deposition we have chemical bath deposition which is also known as solution growth technique. A precursor solution of the target metal ions is complexed by ligands, then anions are added to the solution. The substrate to be deposited is placed in a specific position in the solution, and left until the desired growth is achieved[79]. Chemical Vapor Deposition (CVD) is another chemical deposition method, that involves the thermally induced reaction of a metal-containing molecule on a heated surface. Metal atoms diffuse from a metal-containing precursor, form a stable nucleus and subsequently growth occurs on the metal to be deposited. Hampden-Smith and Kodas describe in detail, with pictures, the CVD process and precursor design[84]. The third chemical deposition method we will discuss is electroplating, which is also called electrodeposition. This is also the procedure which is used on the electrodes described in this thesis. Electrodeposition is a chemical process that is assisted by an electric current. It usually occurs in a solution called an electrolyte which is a solution of the salt of the metal to be deposited in form of submicroscopic metallic particles. A charge transfer occurs during deposition to produce the metal layer in the electrode. The solution is placed in an electrochemical cell, together with an anode and a cathode. Figure 3-1 shows a basic electroplating cell setup. The cathode is the object to be plated and the anode completes the electric circuit and causes a thin film to be deposited on the cathode[85]. Both the anode and cathode materials should be conductive to allow the passage of electric current and completion of the circuit. The anode should also be an inert material to avoid and resist reaction with the metal salt solution[86]. Another essential component of the electrodeposition setup is a power source that provides current or voltage to the e-chemical cell. Electrodeposition is very versatile, and some existing fundamental applications include decorative coatings, wear coating and coatings to prevent corrosion. Although the fundamental applications of electrodeposition are prevalent, new ones will continue to develop in the fields of energy engineering, biotechnology, and nanoelectronics. The development of the procedure in these areas will lead to new and improved material properties[87]. Advantages of electrodeposition include controlled thickness and morphology of deposited material[88], high deposition rates, and inexpensive equipment. The thickness of the film can be controlled by the concentration of the solution, the applied potential or the potential range, and the duration of deposition. The structure of the thin film produced depends on the material properties and preparation conditions. When a coating or film is produced using electrodeposition, it conforms to the surface structure of the surface to be deposited. Hence, its purpose is not to hide cracks and crevices but to actually enhance them. This also increases the surface area of the substrate, and that in itself lends to various application advantages.

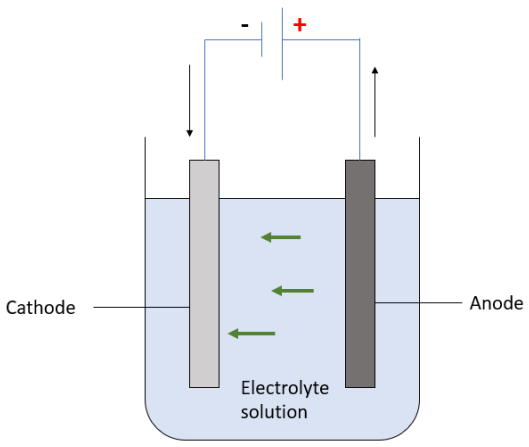

Figure 3-1: Basic setup for electroplating

A special type of the electrochemical deposition process is electroless deposition, which is deposition in the presence of a reducing agent dissolved in the electrolyte and acting as the electron source for the occurring redox reaction. In this method, no external power supply is used[87]. The reaction described is autocatalytic, meaning one of the reaction products is also a catalyst for the same reaction. Some advantages of this procedure are that there is no need for power sources and coatings of uniform thickness are produced. Disadvantages however are low deposition speed and a limited choice of coating metals[86].

3.2 Experimental Procedure and Components

Electrodeposition was chosen in this work over the other deposition methods because of the prospect of realizing a cost-effective biosensing setup. As mentioned earlier It doesn't require expensive equipment unlike most other deposition methods that require some form of a vacuum environment or high reaction temperature. The metal deposited is platinum (Pt), and the substrate being deposited is tungsten(W). The electrodeposition process described in this work resulted from the study of the electrodeposition work done by various other research groups, looking at the deposition parameters, control parameters, solution conditions, and combining and modifying the different studied parameters to ones suitable for my application.

The experimental components are as follows: a working electrode prepared using tungsten; a working electrolyte which is an aqueous solution of 0.002M Potassium hexachloroplatinate(K_2PtCl_6) + 0.1M Perchloric acid ($HCLO_4$), temperature kept at room temperature; Ag/AgCl(sat'd 3M KCl) reference electrode from BASi research products[89]; platinum counter electrode; Gamry Interface 1010E potentiostat for potential control, and a ThinkPad laptop containing Gamry software for recording. Figure 3-2a shows how all experimental components interacted with each other in carrying out electrodeposition. All solutions were prepared using distilled (DI) water and reagents from Sigma Aldrich. The solutions were also thoroughly deoxygenated by purging the cell with nitrogen. Figure 3-2b shows the electrochemical cell used for the electrodeposition procedure. The cell was fabricated in-house by drilling holes, fit for each electrode component and degassing tube, into the cap of a small glass container. The electrodes are characterized using Scanning Electron Microscopy (SEM) analysis and Energy Dispersive Spectrum (EDS) spectrum, carried out by JEOL IT500 scanning electron microscope at accelerating voltages 15kV and magnifications of 2000x and 10000x to show different viewpoints and sizes of the deposited particles.

Cyclic Voltammetry: electrodeposition was carried out on the tungsten electrode using previously described cyclic voltammetry, which is an electrochemical method of cycling the applied voltage between an initial and final voltage value at a set scan rate for a certain number of scans. The working electrode potential was scanned over the range E = -0.1V to +0.1V vs Ag/AgCl at a scan rate of 500mV/s and for 400 cycles, taking about 4 minutes. After deposition, the electrode was rinsed with DI water and allowed to air dry under room temperature. The potential range and scan rate used was selected after studying the scan voltage ranges and rates of other articles on platinum electrodeposition[90], [91]. The number of scan cycles were varied to observe the difference in the surface deposition characteristics, and these differences are discussed under the results and discussion section.

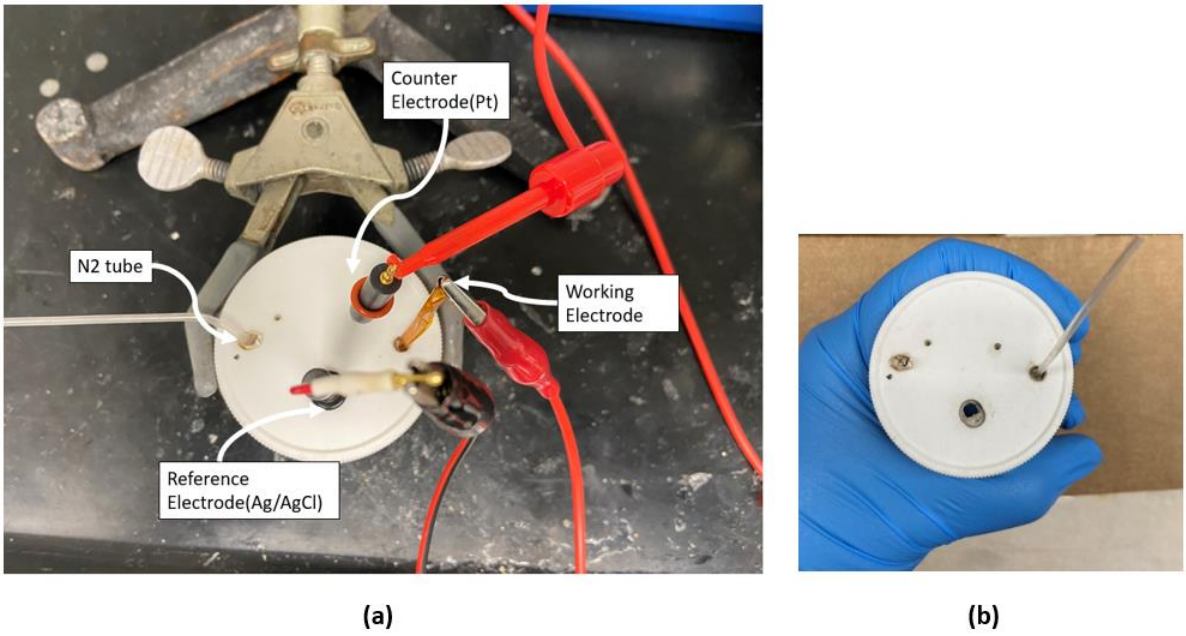

Figure 3-2: (a)Electrochemical cell setup for electrodeposition and dopamine (DA) sensing (b)Aerial view of electrochemical cell

3.3 Results and Discussion

In this work, the aim was to create thin films of platinum with desirable characteristics for dopamine sensing in vitro. Samples of solid state K_2PtCl_6 are dissolved in an aqueous solution of perchloric acid. The potential is cycled over a 200mV range, starting from 0.1V vs Ag/AgCl at a scan rate of 500mV/s. The nomenclature "vs Ag/AgCl" implies that all voltages are referenced to the potential of the Ag/AgCl reference electrode used in the setup. Preliminary experiments revealed that under room temperature and without nitrogen degassing, deposition of the thin film occurred minimally. When nitrogen was introduced, the film thickness and abundance drastically increased on the tungsten substrate. The introduction of Nitrogen to the cell creates an inert atmosphere, and removes oxygen from the electrolyte solution, which is essential in most electrochemical experiments[92]. Oxygen undergoes a reversible one-electron reduction, forming the oxygen radical anion O_2^-. The presence of oxygen in an electrochemical cell can alter the electrochemical response of the analytes. For example, in the article by Elgrishi et al[93], $[Co(Cp)(dppe)(CH_3CN)](PF_6)_2$ undergoes two reversible, one electron reductions under inert atmosphere however with the introduction of oxygen, loses its reversibility because the reduced analyte can transfer an electron to the dissolved O_2 and become oxidized. Based on these studies and observations, all electrolyte solutions used in this study were sparged with nitrogen for about 10 minutes

to remove dissolved O_2 from the cell. After the O_2 is removed, the tubing used for sparging is placed in the space above the solution to blanket it with Nitrogen, keeping any incoming oxygen outside the cell.

SEM analysis shown in figure 3-4a and 3-3a depicts Pt on the surface of the electrode deposited in an electrolyte solution with sparging and without sparging, respectively. The EDS spectrum in Figure 3-4b and 3-3b further verify the presence of Pt from a deoxygenated and non-deoxygenated electrolyte solution respectively. The SEM images show that there is no platinum coating on the electrode deposited in a solution without nitrogen deoxygenation whereas an abundant presence of platinum can be seen in the other electrode. The EDS spectrum also reveals the same information. In Figure 3-5b (EDS spectrum of Pt coated) however, the EDS spectrum shows a reasonable amount of tungsten at the point 'spectrum 21'. This can be attributed to the accelerating voltage value. The higher the accelerating voltage used in an SEM, the more likely fine details of the surface materials disappear and deeper material attributes are detected. If a voltage of 5kV was used as the accelerating voltage, the spectrum would register significantly more Platinum than tungsten. However, at lower accelerating voltages, there is less of a distinction in the produced electron image between the cell and the substrate, with both of them being displayed at about the same brightness level[94].

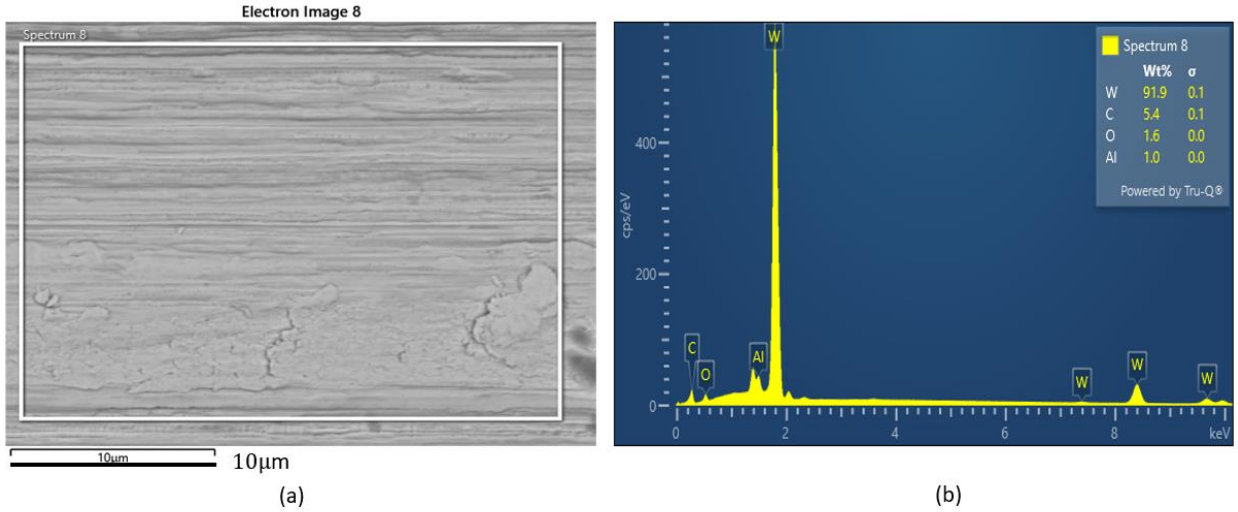

Figure 3-3: (a) SEM electron image of Pt deposition in electrolyte solution without N_2 bubbling (b) corresponding EDS spectrum

Another important factor that affects the thin-film deposition is the number of cycles. The effect of the number of deposition cycles is observed by comparing Figure 3-4 and Figure 3-5, which represent the SEM analysis of the electrode using 20 cycles and using 300 cycles respectively. We notice that there are a few platinum particles on the latter electrode, and a more film-like structure of platinum on the later electrode.

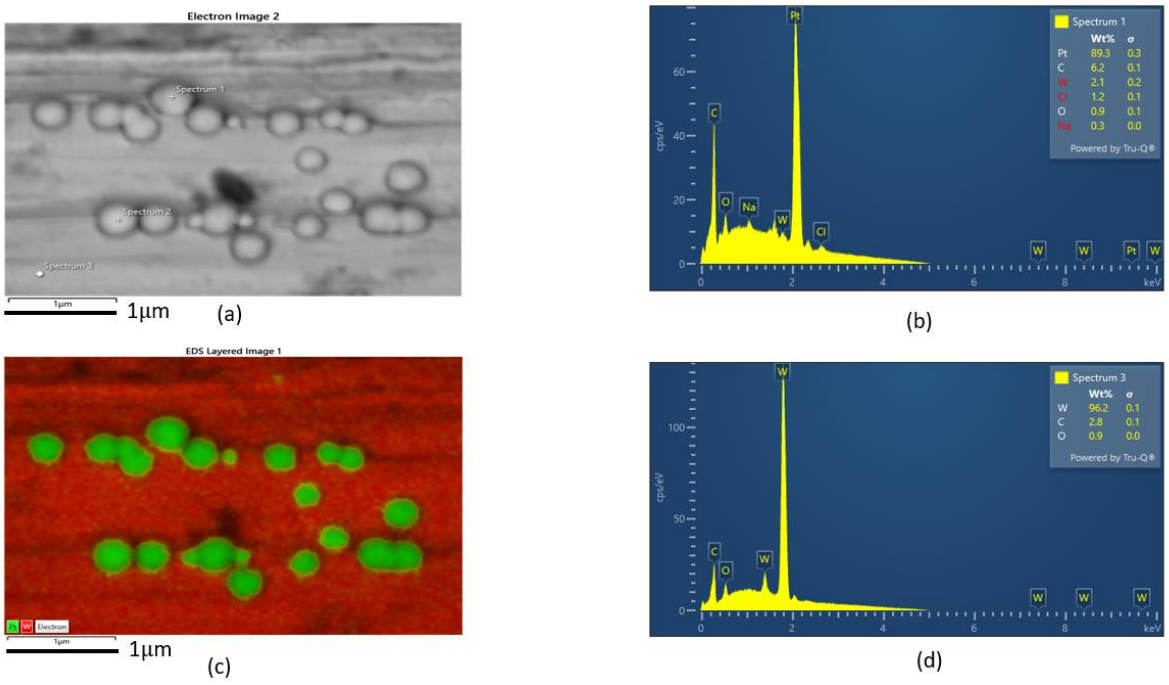

Figure 3-4: (a) SEM electron image of Pt electrodeposited W electrode in electrolyte solution with N2 bubbling, 10 voltammogram deposition cycles (b) EDS spectrum of point 1 (c) EDS Layered Image showing Pt particles against W background (d)EDS spectrum of point 3

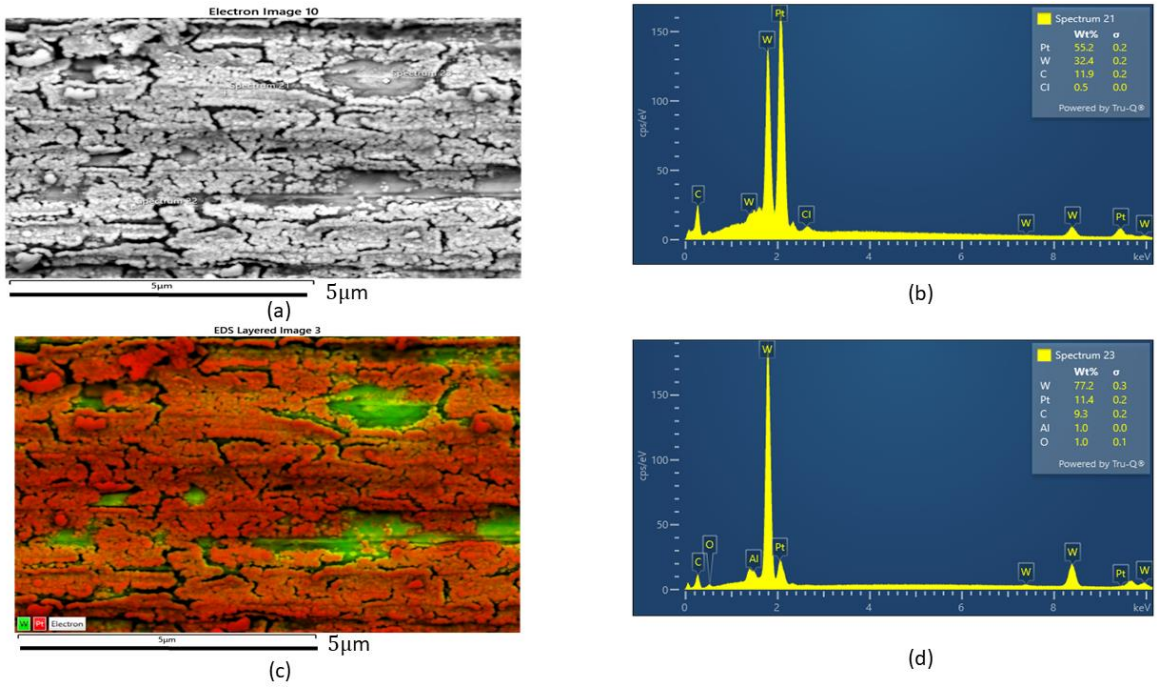

Figure 3-5: (a) SEM electron image of Pt deposited W electrode in electrolyte solution with N2 bubbling, 300 voltammogram deposition cycles (b) EDS spectrum of point 21 (c) EDS Layered Image showing Pt particles against W background (d)EDS spectrum of point 23

The electrodeposition of Pt from $PtCl_6^{2-}$ involves four electron reduction processes; these can be the one step Pt(IV) –> Pt(0) or the two step Pt(IV) -> Pt(II) ->Pt(0)[95]. With each subsequent scan, as shown in the voltammogram in Figure 3-6, new redox peaks increase with an increase in number of cycles, indicating platinum nanoparticle growth.

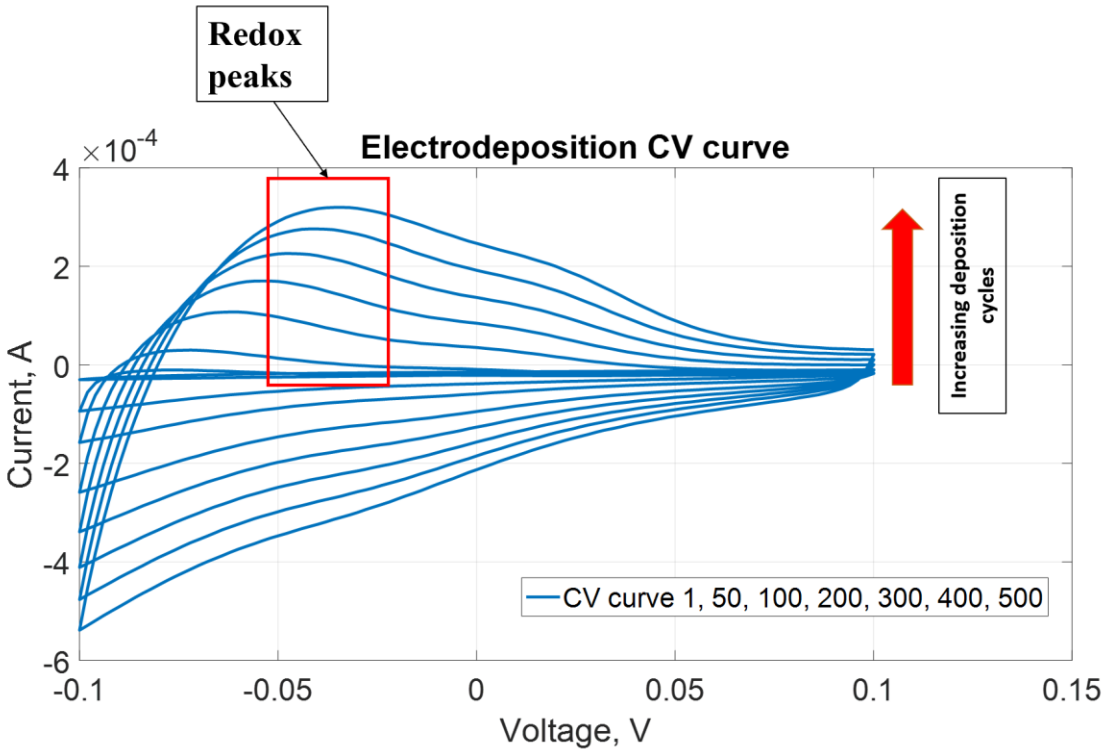

Figure 3-6: Electrodeposition Voltammetry Curve

SEM Characterization using the JEOL IT500 happens when an electron beam focused using a combination of lenses and apertures hits the surface of the sample. The sample is mounted on a stage in the chamber area of the SEM as shown in Figure 3-7. The electron interacts with the sample to produce different signals which are detected by their appropriate detectors which passes the signals onto an analyzer for data display and analysis[96]. The EDS spectrum and layered image is also produced using the SEM equipment and is used to determine the chemical elements present on a sample and estimate their abundance relative to each other. Figure 3-5 (c) and (d) is an example of an EDS layered image and an EDS spectrum respectively, showing the Pt composition of the electrode.

Figure 3-7: JEOL IT500 Scanning Electron Microscope Chamber

4 CHAPTER 4- Dopamine Sensing, Measurements, and Comparison

The main point of the work presented in this thesis is to demonstrate the demonstrate the dopamine sensing capabilities of a platinum fiber electrode and present the basis for an in-vivo dopamine sensing platform that can lend itself to clinical applications. Neurotransmitters are important for a variety of functions in the nervous system as they deliver messages in the form a nerve impulse from the brain[97]. Dopamine (DA), which is a type of neurotransmitter, is used by the body and the nervous system to send messages between nerve cells. It plays an important role in reward and movement regulation in the brain[98]. In its reward role, dopamine production happens in the ventral tegmental area (VTA) in nerve cell bodies. For its motor functions, substantia nigra cell bodies are the pathways responsible for the production and discharge of DA into the stratium. Calabresi et al discusses how DA influences different forms of synaptic plastic changes associated with human pathological conditions like addiction or dyskinesia[99]. DA is transported to different areas of the brain using some major pathways known as mesostriatal, mesocortial, and mesolimbic pathways[100]. The innervations that originate from each of these pathways are responsible for many effects that occur when the DA system is activated. For example, the VTA is connected to the rest of the brain through the mesolimbic pathway, and it is central to the brain reward system[101]. Studies show that an abundance of dopamine could be linked to some cancers, while a scarcity could be associated with Parkinson's disease and depression[102]. It is therefore essential to have a platform for sensing dopamine levels in the brain. This will help with diagnosis of various diseases and possibly early treatment. Given the importance of dopamine, efforts from different research groups have been focused on implementing fast and reliable methods for its determination[97], [103]–[105].

With the development of various methods for DA detection comes the development and investigation of sensing materials. This investigation is also broadened by the advancements in nanotechnology. Broad categories of materials that have been developed for DA sensing include metals, metal oxides, and polymers. Metals have particularly emerged as promising candidates for DA sensing due to their unique properties. Metal examples that have been explored include platinum, gold, palladium, and titanium. Some materials that can be found in different DA sensing papers include graphene, carbon nanofibers, platinum, gold nanoparticles, to name a few[34], [103], [106], [107]. A lot of research is also focused on modifying the surface of electrodes in the case of electrochemical sensing to make the electrodes have a higher sensitivity towards DA. An example of this concept is demonstrated by Lupu et al. [108] who developed an electrochemical sensor with a platinum electrode base, modified with hybrid inorganic-organic coating. The modified electrode was used in the detection of 4-nitrophenol and dopamine. The inorganic-organic coatings were prepared by electrochemical methods using various configurations. Another example of surface modification is presented in the paper by Ouellete et al.[104] The team functionalized commercially available electrodes by depositing a thin film of pre-formed gold nanoparticles. The functionalization solution also included DNA and polymers. The paper reports an increase in dopamine oxidation current by 92%.

The cited papers [97], [105], [106] describe electrochemical methods of detecting dopamine and are relevant references as that is the method for DA sensing presented in this work. In particular, Cyclic Voltammetry and Differential Pulse Voltammetry (DPV) will be used in detecting DA in-vitro. Cyclic Voltammetry is a technique used to detect neurotransmitters and it has been used, including other techniques, to detect dopamine, noradrenaline, serotonin, and indoleamine with carbon fiber electrodes. This technique is effective because neurotransmitters are electro active and oxidize at a low voltage. The detection of dopamine in-vitro is influenced by different parameters such as buffer solution, concentration, electrode material, and voltammetry cycle number. In this work, the concentration,

electrode material, electrode surface area, and voltammetry cycle number were studied in relation to how they affect the resulting DA sensing current. The different working electrodes compared include 50um diameter W/Pt deposited electrode and two differently sized pure Pt electrodes. Surface area of the electrodes is an important factor to discuss because the surface area involved in a reaction generally determines the rate of the chemical reaction. For instance, a larger surface area favors the adsorption of more analyte molecules, which increases the response of the sensor and consequently improves sensitivity.

4.1 Experimental Chemicals:

Dopamine hydrochloride and 1X Phosphate Buffer Solution (PBS) pH 7.4 buffer were purchased from Sigma Aldrich (St. Louis, Missouri, USA). All chemicals were used without further purification. Distilled water was always used to prepare any required aqueous solution. DA stock solution was prepared using small amounts of PBS before being diluted to target concentration in more PBS.

4.2 Electrochemical Measurements:

The electrochemical experiments were carried out in the lab designed single compartment electrochemical cell made from a 50ml glass container and custom lid with drilled holes for each component electrode, as described in Figure 3-2. A Gamry Potentiostat coupled to a PC running the Gamry software was used in potential control and current recording. The electrodes used were as follows: Pt deposited working electrode as described in Chapter 3, 50um diameter 99.99% purity Pt (surepure chemetals), 127um diameter 99.99% purity Pt (surepure chemetals), Ag/AgCl (sat'd 3M KCl) reference electrode (Sigma Aldrich), and Platinum counter electrode (BASi research products). All experiments were carried out at room temperature and at a neutral pH of 7.4. Before each experiment, the electrodes were rinsed with distilled water and wiped dry. The DA buffer solution was also bubbled with pure N_2 gas pre-measurements and blanketed with the same gas during experiments.

4.3 Electrode Preparation:

To convert the multimaterial fibers to electrodes with electrical connection points, the fiber was stripped ~0.5" at both ends, and one end was connected to a copper wire using flash-dry silver conductive paint (spi supplies) and an epoxy for securing the connection. This illustration is seen in Figure 4-1. The electrode is then left to dry out for about a day, and the copper wire serves as the connection points for the electrical clips. To prepare the pure platinum electrodes, the wires were inserted into a PC/Cu fiber, with its Cu component stripped out as described in Chapter 2.

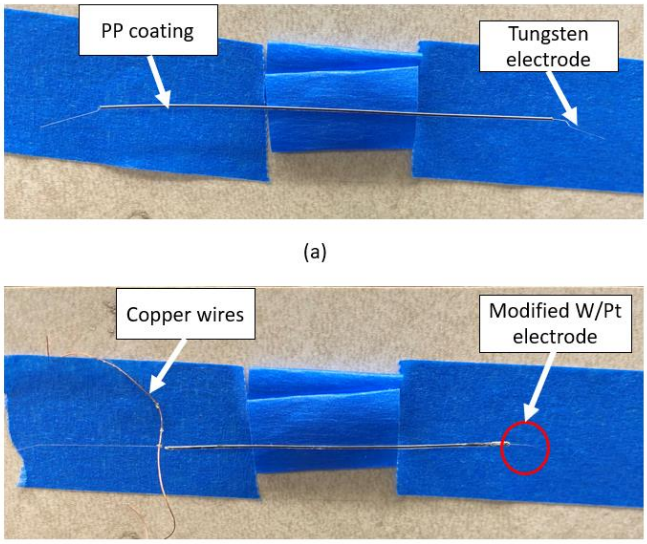

Figure 4-1: (a)picture of PP/W fiber with stripped ends exposing tungsten(W) electrode (b)picture of the connected tungsten(W) electrode using copper wires for electrochemical experiments.

4.4 Results and Discussion

All plots presented as results were generated using MATLAB. Dopamine sensing was carried out by cycling the potential between -0.1V and 1V for two or three cycles to allow for stability of the sensor signal. The cycle presented is the latter of all the cycles recorded i.e., the second or third cycle, depending on the applied scan rate. Figure 4-3a, c, and e present the CV results for dopamine sensing in PBS pH 7.4 solution using the electrodeposited platinum electrode, 51µm pure (99.99%) platinum electrode, and 127µm pure (99.99%) platinum electrode, showing different scan rates (ranging from 100mV/s to 2V/s). The voltammogram in Fig 4-3d shows the oxidation of 5mM dopamine solution using the 50um W/Pt deposited electrode at a scan rate of 500mV/s. The oxidation peak during the positive sweep appears at potential value 0.83V with a corresponding current value of 0.16mA and the reduction peak slightly appears during the negative sweep at potential 0.06V with a corresponding current of -43.2µA. When the scan rate is reduced to 100mV/s as shown by the blue line in the aforementioned figure, the shape of the voltammogram slightly changes with a higher reduction peak and lower oxidation peak value (-6.9µA and 88.79µA respectively). This, as well as Fig 4-3 a and c depicting a wider range of scan rates shows that faster scan rates lead to higher detected oxidation peaks. Observing this voltammogram confirms the conclusion from various research groups that dopamine oxidation is a quasi-reversible reaction[109]. DA oxidizes to dopamine quinone, and is associated with the reaction described in figure 4-2 which is a two-electron transfer oxidation of dopamine[110]–[113].

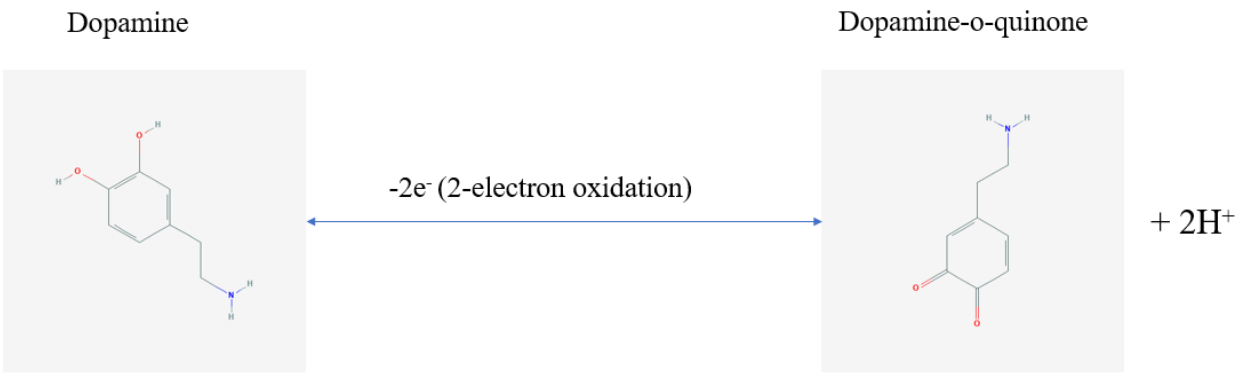

Figure 4-2: Dopamine 2-electron oxidation to dopamine-o-quinone

The electrochemical behavior at the 127µm working electrode is depicted by the voltammogram shown in Fig 4-3a and b, scanned between -0.1V and 1V. At a scan rate of 500mV/s as shown by the red line, an oxidation peak value of 84.7µA from the positive scan occurs at 0.7V, and a reduction peak value of -14µA occurs at 0.06V. Lower oxidation and higher reduction peak values are also observed for a lower scan rate, as described for the Pt deposited electrode, confirming the assertion that faster scan rates result in higher oxidation peaks. Comparing the oxidation peak values at the 127µm pure Pt electrode to those at the Pt deposited electrode shows a higher resulting value form the Pt deposited electrode. This means that the sensitivity of this electrode is higher than that of the 127µm diameter pure Pt electrode. This attests to the ability of the platinum deposited electrode to properly sense DA and although the 127µm diameter electrode has a larger surface area than the other, the deposited electrode still shows better sensitivity to DA than its pure Pt wire counterpart. This promising result will encourage the study of DA sensing using Pt electrodes, exploring electrodeposition as a cost-efficient and effective method for their preparation.

To examine the effect of the number of deposition cycles on dopamine sensing, I varied the number of deposition cycles for one of the electrodes and recorded its voltammogram in 5mM DA and PBS solution. Fig 4-4 compares the 100mV/s voltammograms of a 500-cycle deposited Pt electrode, a 300-cycle deposited Pt electrode, and a 127µm diameter pure Pt electrode to each other. The results show that the sensing capabilities of the 300-cycle deposited Pt electrode (red line) is lower than that of the other two electrodes (blue and yellow lines). From this observation, we can infer that the higher the number of deposition cycles applied to the base electrode (tungsten in this case), the better the sensing characteristics of the electrode.

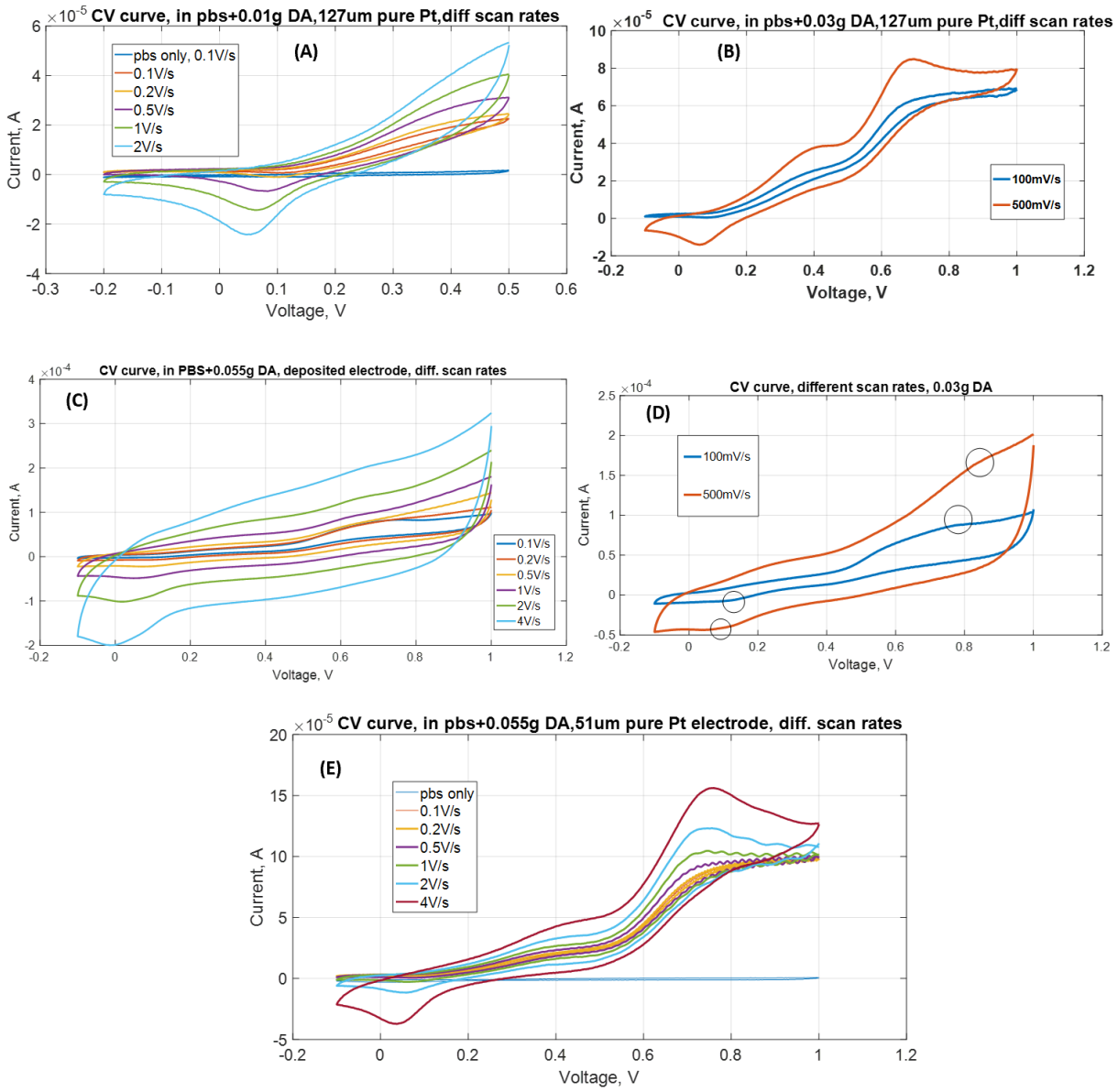

Figure 4-3: (A)Cyclic Voltammograms of 127µm pure Pt electrode in 5mM DA solution; scan rates 0.1V/s,0.2V/s,0.5V/s,1V/s, and 2V/s; (B). Cyclic voltammogram of 127µm pure Pt showing scan rates 100mV/s(blue) and 500mV/s(red); (C)Cyclic Voltammograms of W/Pt modified electrode in 8.5mM DA solution; scan rates 0.1V/s,0.2V/s,0.5V/s,1V/s, and 2V/s (D). Cyclic voltammogram of 500-cycle W/Pt modified electrode in 5mM DA showing scan rates 100mV/s(blue) and 500mV/s(red); (E). Cyclic Voltammogram of 51um pure Pt electrode in 8.5mM DA solution, scan rates 0.1V/s – 1V/s

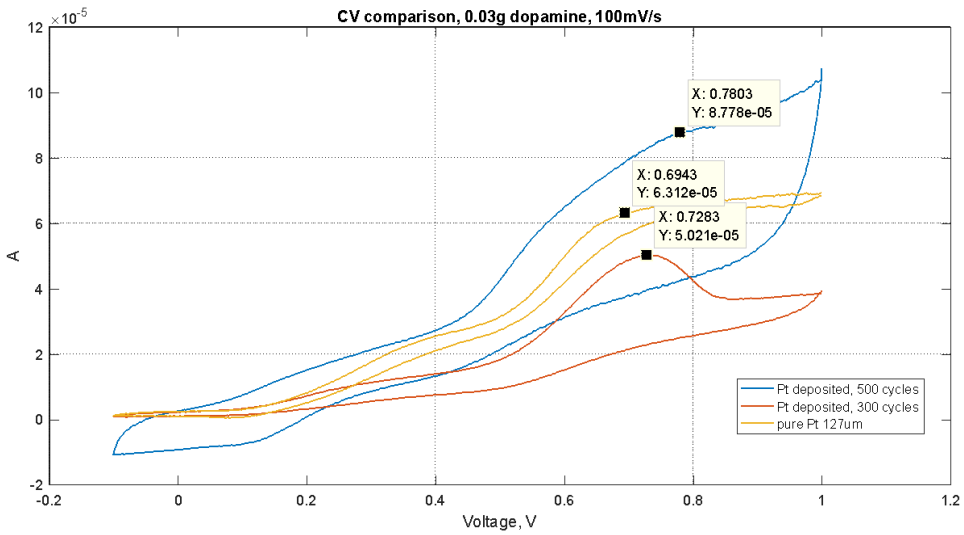

Figure 4-4: Cyclic Voltammogram comparing current(A) results at (red)300-cycle deposited Pt electrode, (yellow)127um diameter pure Pt electrode and, (blue)500-cycle deposited Pt electrode in 1X PBS solution containing 5mM of DA; voltammogram recorded from -0.1V to 1.0V

Differential Pulse Voltammetry (DPV) is also used in dopamine sensing because studies show that DPV is a more sensitive method of sensing, allowing direct analyses at the parts per billion level[114]. DPV involves applying a constant amplitude pulse potential, while increasing the pulse's potential with time. This means each subsequent pulse is higher than its predecessor, although each pulse is the same size[115]. The current output will increase until the redox potential of the electroactive analyte is reached after which the current will decrease. Measurements are taken just at the start and at the end of a potential pulse and the difference between the two currents is plotted with the cell's potential staircase. The potential range used for the DPV in this work is -0.3V to 0.7V. The DPV in the electrochemical cell with dopamine solution was recorded in different dopamine concentrations, for four working electrodes to determine their sensitivities. Fig 4-5a shows the DPV recorded at the 500-cycle deposited Pt electrode in 1X phosphate buffer solution containing 1.7-8.5mM of DA. The DPV shows that as the DA concentration increase, the current output increases. It also shows a slight drift in the redox potentials for each DA concentration. This can be attributed to the inconsistency on the deposited electrode's surface. The linear dependence of the peak current on the analyte concentration is characterized by the equation I(µA) = 5.64x + 8.576 where 'x' represents the DA concentration, with a correlation coefficient R^2 = 0.9867. The sensitivity of this sensor can be calculated from the slope of the linear fit plot as seen in Fig 4-5b; this value comes to 5.64µA/mM. The DPV recorded at the 127µm pure Pt electrode and the 300-cycle deposited Pt electrode for the same DA concentrations and their corresponding linear fit is also shown in Fig 4-6 and Fig 4-7 respectively. The linear fit equation for the 127µm pure Pt electrode is I(µA) = 5.04x – 6.506 where 'x' represents the DA concentration, and the correlation coefficient R^2 is 0.9874. It's corresponding sensitivity value which is calculated from the slope of the plot is given as 5.04µA/mM. This value is lower than the 5.64µA/mM sensitivity value gotten for the deposited platinum electrode. This shows that the deposited platinum electrode is more sensitive to DA in the DA and PBS solution when compared to the 127µm pure Pt electrode.

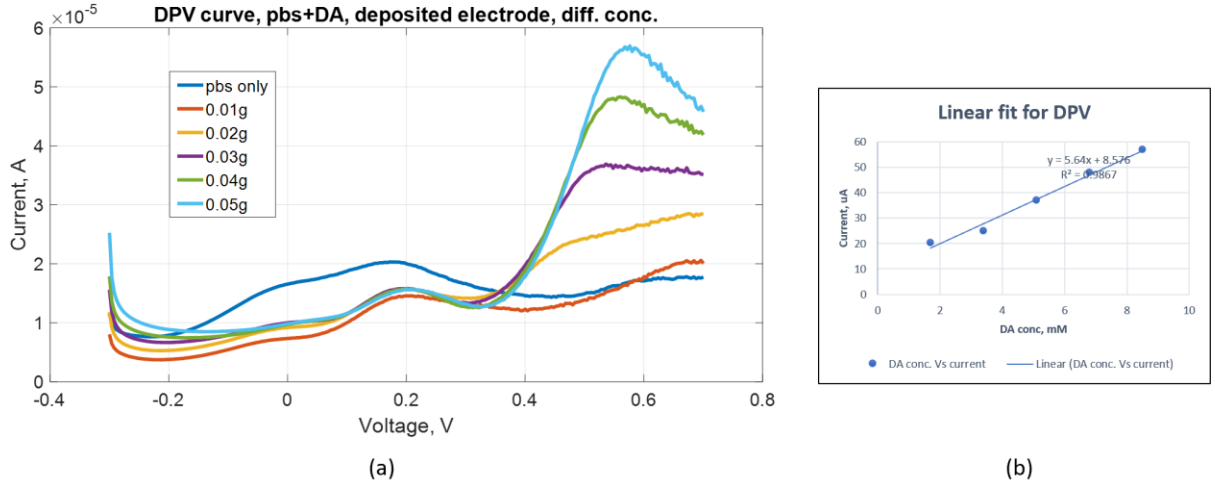

Figure 4-5: (a)Differential Pulse Voltammogram recorded at the W/Pt deposited electrode w/500 deposition cycles recorded in 1X PBS solution of pH 7.4 at different DA concentrations ranging from 1.7 to 8.5mM, pulse range -0.3V to 0.7V (b)corresponding linear fit plot for the DPV results.

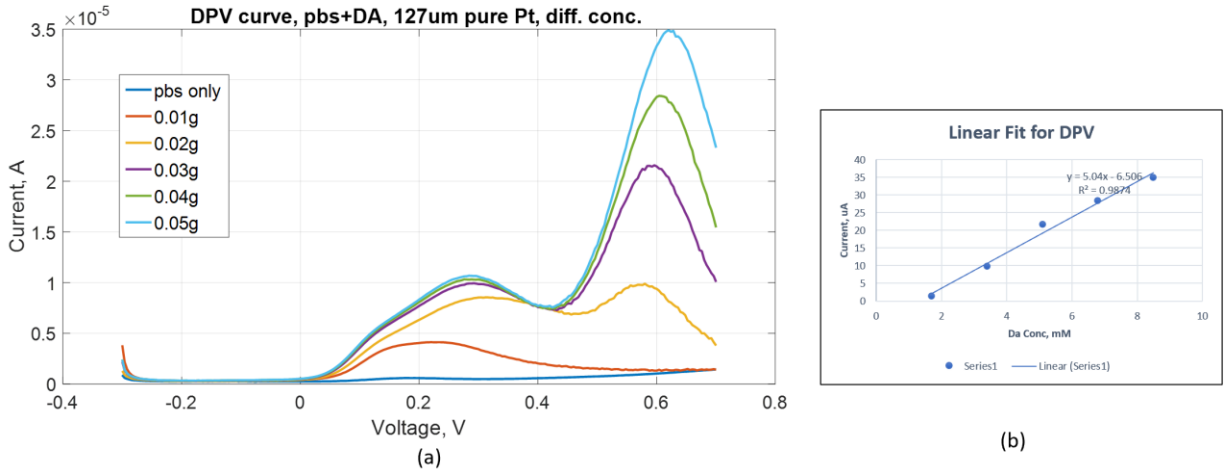

Figure 4-6: (a)Differential Pulse Voltammogram recorded at the 127um diameter pure Pt electrode recorded in 1X PBS solution of pH 7.4 at different DA concentrations ranging from 1.7 to 8.5mM, pulse range -0.3V to 0.7V (b)corresponding linear fit plot for the DPV results.

The third Differential Pulse Voltammogram that we studied is that for the 300-cycle Pt deposited electrode. Its voltammogram is displayed in Fig 4-7, as well as it's linear fit plot. The linear dependence equation is derived as I(µA) = 2.93x + 8.52 where 'x' represents the DA concentration, and it has a correlation coefficient of R^2 = 0.9941. Its sensitivity value gotten from the plot's slope is 2.93µA/mM. Out of the three electrodes discussed so far, 2.93µA/mM is the lowest sensitivity value, meaning that the 300-cycle deposited Pt electrode is the least effective in sensing dopamine. The last electrode that was worked with is the 51µm diameter pure Pt electrode. This electrode was chosen to provide a reference Pt electrode with the same dimension as the W/Pt modified electrode. It's voltammogram and linear fit plot are shown in Fig 4-8. The linear dependence equation gotten from its linear fit is I(µA) = 3.54x – 3.68 and its correlation coefficient R^2 = 0.9945. The sensitivity value for this electrode is gotten from its linear fit's slope and is 3.54µA/mM. Table 4-1 compares the sensitivity values from the four electrodes studied. From this comparison, we see that the W/Pt deposited electrode with the highest number of deposition

cycles (500 cycles) has the highest sensitivity value, followed by the 127µm diameter pure Pt electrode, after which we have the 51µm pure Pt electrode, and the least sensitivity value which comes from the Pt deposited electrode with the lesser amount of deposition cycles (300 cycles). This result shows how the number of deposition cycles affects the sensing capabilities of an electrode and shows that deposition of Pt produces better sensing results than the use of Pt electrodes with larger diameters. This implies that instead of purchasing Pt wires which are expensive, the cost-effective electrodeposition preparation method can be used to build a cheaper DA sensing platform.

Table 4-1: Working electrodes (WE) used in the experiments and their corresponding sensitivity values is uA/mM

Working Electrode Type	**Sensitivity value(µA/mM)**
500-cycle W/Pt modified electrode	5.64
300-cycle W/Pt modified electrode	2.93
51um diam. pure Pt	3.54
127um diam. Pure Pt	5.04

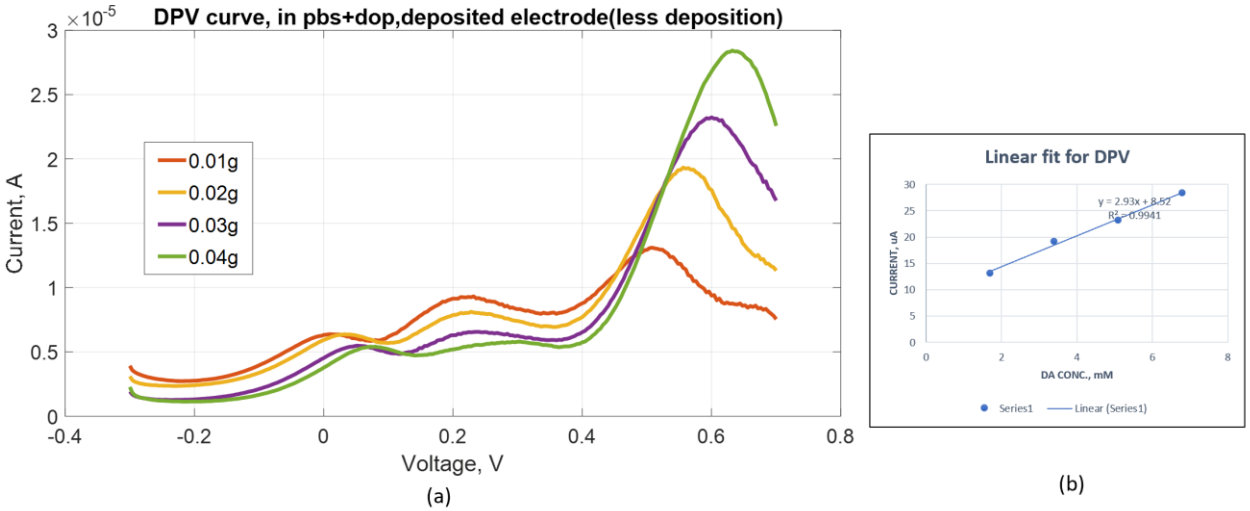

Figure 4-7: (a)Differential Pulse Voltammogram recorded at the W/Pt deposited electrode w/300 deposition cycles recorded in 1X PBS solution of pH 7.4 at different DA concentrations ranging from 1.7 to 7mM, pulse range -0.3V to 0.7V (b) corresponding linear fit for DPV results.

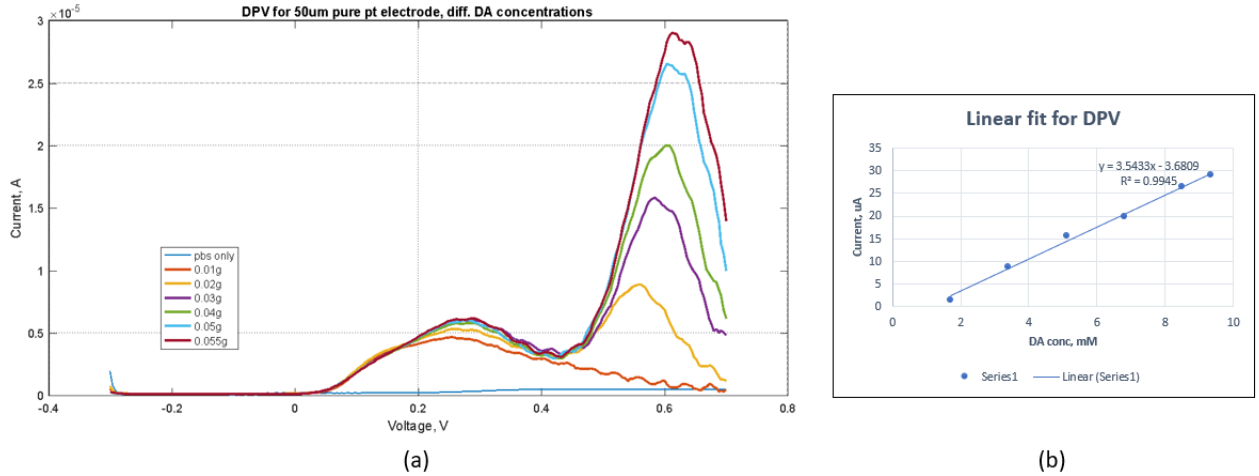

Figure 4-8: (a) Differential Pulse Voltammogram recorded at the 51µm diameter pure Pt electrode recorded in 1X PBS solution of pH 7.4 at different DA concentrations ranging from 1.7 to 9.35mM, pulse range -0.3V to 0.7V (b)corresponding linear fit for DPV results

5 Conclusion and Future Outlook

5.1 Conclusion

The point of this thesis was to describe efforts towards biosensing, specifically the sensing of dopamine (DA) which is a neurotransmitter in the brain. The basics of biological sensing and the specific sensing method used (electrochemical sensing) were explained to aid the reader in understanding the rest of the work discussed. Electrochemical sensing was described as a sensing procedure that integrates electronics and the chemical composition of the sensed analytes. This method is normally carried out in an electrochemical cell containing three electrodes serving different purposes and the sensing solution. The advantages of electrochemical sensing such as its ability to be miniaturized and it's cost effectiveness were also discussed.

Multimaterial fibers, which are the basis of the sensing electrode used in the work detailed in this paper were described along with their fabrication methods, applications, and functionalities. The invention of multimaterial fibers allows for the integration of electronic and optoelectronic functionalities into a bare optical fiber. The electronic functionalities were discussed as relating to biomedical applications, although they can be applied elsewhere. The specific multimaterial fiber used in this work, which is a tungsten electrode embedded in an optical fiber core with Polypropylene cladding was also mentioned, and it's drawing process was described. We mentioned important fiber parameters which include its diameters (electrode diameters and coating diameters) and material composition. Apart from the discussion of the biosensing and fiber basics, the two important aspects that this thesis focused on is electrodeposition of electrodes and DA sensing using electrochemical methods.

Electrodeposition as described in Chapter 3 is a deposition procedure involving applying potentials at a working electrode in an electrochemical cell containing the salt solution of the metal to be deposited. In our case, we described the deposition of platinum (Pt) onto a tungsten(W) substrate using Cyclic Voltammetry, which is one of the electrochemical methods, between two set potentials. The platinum salt used in the electrodeposition procedure is K_2PtCl_6(potassium hexachloroplatinate), and the amount of deposited metal was controlled by the number of deposition cycles. The deposited electrodes were characterized using SEM images and EDS plots. The characterization shows the surface properties of the electrodes before and after the deposition procedure.

Finally, we discussed the sensing of DA in a Phosphate Buffer solution (PBS) using electrochemical methods, specifically cyclic voltammetry or CV and Differential Pulse Voltammetry or DPV. The working electrodes used in this study were the Pt deposited electrodes and pure platinum wires embedded in a fiber structure. This work studied the voltammograms generated for each of the electrodes introduced into the DA solution. The voltammograms show information relating the concentration of DA in solution to the current output. The voltammograms also change corresponding to scan rates, with higher scan rates yielding higher more pronounced oxidation peaks and lower reduction peak values. The CV plots presented in Chapter 3 display a range of scan rates for some of the electrodes studied and shows their variation effects on the sensing capabilities of the electrode. A linear fit curve was produced using the DPV voltammograms and the sensitivity values for each of the electrodes was calculated from the slope of the linear dependence equation. Table 4-1 shows that the 500-cycle W/Pt modified electrode has the best sensitivity, and the 300-cycle W/Pt modified electrode has the worst sensitivity of all four electrodes. The fabrication and implementation of these multimaterial fibers shows promise for a DA sensing platform, made cost-effective by the electrodeposition process, and made interesting for in-vivo applications by the small size of its electrode.

5.2 Future Outlook

Positive and insightful discoveries about biosensing were made during the course of this research. The dopamine sensing done in this work was carried out using multimaterial fiber electrodes and electrochemical sensing methods. The results prove that dopamine can indeed be sensed using platinum material on a flexible electrode such as fiber electrodes. Further discussion also showed that the tungsten fiber electrode used in the experiments can been woven into a 2D textile like item. This implies that the sensor can be implemented as a woven textile platform, allowing for wearable and convenient applications. The use of electrochemical sensing also makes miniaturization of a developed platform easier as it is the easiest biosensing method to simplify because of its use of simple equipment and its lack of need for complex experimental environments. However, there is more work and testing that should be done to attain the motivating goal, which is developing a sensitive and selective portable flexible sensing platform for in-vivo sensing of dopamine.

Some additional experiments that can be carried out to create a more stable sensing system and produce better results include the following: variation of the electrodeposition cycles for a more stable and well covered platinum surface on the tungsten wire. A larger platinum surface area would lead to better sensitivity of the electrode; The electrodeposition process and dopamine sensing could also be carried out in a more controlled environment. The experimental conditions used in this research although functional were not the most ideal. Carrying out the experiments in ideal environments such as in a nitrogen glovebox to always ensure inert atmosphere or in a commercially available electrochemical cell to ensure tight seals on all electrode entry ports could lead to better and more stable current output from the cyclic voltammetry process; a higher purity Nitrogen gas or a heavier inert gas such as Argon can also be used in the experiments to produce different results. Observations of the results would be made to see if any positive or negative changes occur; an additional experiment that can be carried out is testing the selectivity of the developed sensor. This work primarily focuses on dopamine (DA) sensing without any intentional interference from other chemicals. Introducing other chemicals that naturally occur alongside dopamine such as Ascorbic Acid (AA) would help in determining the platform's selectivity and adjusting its sensing materials based on selectivity test results. The repeatability of the proposed sensing platform can also be tested by taking the average of multiple resulting voltammogram plots from DA sensing and repeating similar sensing experiments on different days to study the viability of the sensing electrode.

Finally, looking forward to in-vivo applications, the use of electronic multimaterial fibers can lead to the combination of the cyclic voltammetry process and electrical stimulation of the brain for release of chemicals. This reduces the number and size of equipment needed for a set of experiments leading to more portable and cost-effective experimental procedures.

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