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Molybdenum Disulfide-Conducting Polymer Composite Structures for Electrochemical Biosensor Applications

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for Electrochemical Biosensor Applications

by

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ABSTRACT

Lactic acid is widely existing in human bodies, animals and microorganisms. Recently, using biosensor to detect the concentration of lactic acid and diagnose disease have attracted great research and development interests. Nanocomposites is one of the best material used for biosensor because their wonderful conductivity, optical and electrochemical properties. In the study, MoS_2 and polypyrrole (PPY) are used for the composite material electrode. To determine whether lactate oxidase (LOD) was helpful for the biosensor's detective properties, both PPY-MoS_2 film with LOD and PPY-MoS_2 film without LOD are being tested. The fourier transform infrared spectroscopy (FTIR) and Raman spectroscopic techniques have been used to understand the chemical bonds in the nanocomposite film. The X-ray diffraction (XRD) technique has been performed to understand the crystallographic structure of the MoS_2-PPY film. The morphologies were confirmed by scanning electron microscopy (SEM). The UV-vis spectroscopy has been used to determine the band structure of composite film. Cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) were used to analyze in different concentration of solution, under different scan rate to obtain stability and work efficiency. These results were compared with PPY-MoS_2 film with and without lactate oxidase conditions. The chronoamperometric technique has been used to detect the concentration of lactic acid.

CHAPTER 1. INTRODUCTION

1.1 Biosensor

Biosensors are important analytical devices to analyze and determine the concentration of biological analytes such as biomolecules, microorganisms and biological structures [1]. The devices comprise of a signal transducer, biological element (sensor) that detects an analyte and produces an electronic signal as well as a signal reader. On the other hand, transducer component is used in the conversation of the recognition events into the measurable signal. The unique aspect of the biosensor is that the two components are integrated into a single sensor (figure 1)[2]. This unique combination allows an individual to measure the targeted analyte without the use of reagents [3].

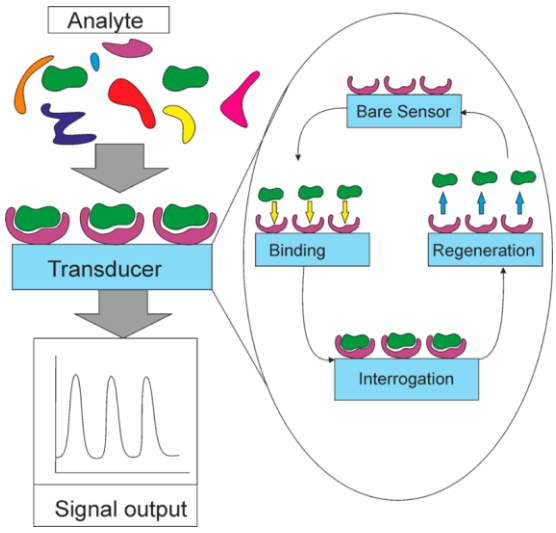

Figure 1. The schematic of biosensor with binding, reaction and signal output. (reproduced with permission from American Chemical Society on 21st Oct) [2].

When the bio-element reacts with the analyte to be investigated, the resultant response is normally converted into electrical, thermal or optical signals using the transducer to quantitatively

determining the complex biochemical parameters of the analyte. This can be achieved by yielding an electrical signal such as current or voltage, which is proportional to the analyte concentration. In the clinical field, biosensors are increasingly being applied for detection and fining the concentration of the neurotransmitters, glucose, cholesterol etc. For example, modern biosensors can directly measure the concentration of glucose in a blood sample by simply dipping it into the sample. This is opposed to traditional analytical methods that required a sample to undergo several processes before sensing. It enhances the simplicity and speed of measurement.

There are different types of biosensors some of which include electrochemical biosensors, potentiometric amperometry biosensors, calorimetric biosensors and optical biosensors. For example, calorimetric biosensors analyze the concentration of biological analytes through the heat of absorption and heat of release during a reaction between an analyte and a bio-element. Potentiometric biosensors work by measuring the electrical potential produced due to a change in the distribution of electrons. Similarly, optical biosensors work by measuring the light absorbed or produced during a reaction [4].

On the other hand, electrochemical biosensors are simple biosensor devices which particularly employ the use of redox reactions in determining and quantifying the presence of an analyte. The chemical information is converted into measurable electrical signals like the current or voltage. For example, the oxidation and reduction reactions involving the biological element and the analyte can result in the generation of current which then flows through the potential difference between two electrodes. The current can be measured to quantify the analyte being analyzed. Unlike other biosensors such as optical biosensors, electrochemical biosensors have fewer drawbacks and have more stable output, faster response, increased sensitivity and lesser interferences. This particularly makes them more suitable for various biosensors. Various

techniques are (electrochemical, optical, surface acoustic wave etc.) used to detect biosensor as shown in Table 1[5].

Table 1. Classification of biosensor and types of signal used to detect the analyte (reproduced from Springer with Permission on 21st Oct, 2016) [5].

Signal transduction	
Electrochemical	amperometric conductimetric impedimetric potentiometric
Optical	absorption fluorescence/phosphorescence bio/chemiluminescence reflectance raman scattering refractive index
Mass sensitive	surface acoustic wave biosensors cantilever biosensors
Thermometric	
Recognising Biomolecule	
Antibodies (Immunosensors)	monoclonal policlonal
Protein Receptors	metabotropic receptors ionotropic receptors
Whole Cells	microbial sensors mammalian cells tissue
Nucleic Acids	hybridisation low weight compound interaction
Enzymes	

The main materials used in the construction of electrochemical biosensors include metal oxide, carbon nanotube, conducting polymer, graphene, dichalcogenide, quantum dots, gold & silver nanoparticles, and carbon among others. Metal oxides are semiconductors made out of a metal sandwiched between an insulator, semiconductor substrate and the oxide of a substrate. A wide range of metal oxides are currently being used in the construction of biosensors. Some of the common metal oxides widely used in electrochemical biosensors include molybdenum oxide [6], iron oxide [7], zinc oxide [8], titanium oxide [9] and aluminum oxide [10] among others. Generally,

metal oxides nano-materials are used in electrochemical biosensors due to their novel electro-catalytic behavior, high detection sensitivity and selectivity [11].

Carbon nanotube (CNT) is another important member of the family of nanomaterials that is increasingly being used in the manufacture of modern electrochemical biosensors. The carbon nanotubes has larger surface areas, excellent electrical conductivity and improved electron transfer reaction properties. According to Haynes et al [4], CNTs are also preferred for biosensors applications due to their excellent biocompatibility, unique tubular structure and the presence of modifiable sidewalls that particularly make them have the ideal construction of high performance electrochemical biosensors. Generally, electrochemical nano-biosensors mainly use CNTs as the preferred transducers due to their higher analytical performances and detection capabilities. However, although the carbon nanotube sensors are still widely used in various biosensing applications, they are not as selective as expected unless their functionality is enhanced by other chemicals, which makes the process more complex with expensive manufacturing process.

Similarly, grapheme is also a powerful nano-material that is currently being used in widely range of biosensor applications. The material particularly provides high thermal conductivity, elasticity and better mechanical strength. However, graphene also has a major limitation attributed to its poor dispersion particularly in aqueous medium. Additionally, the graphene based field – effect-transistor (FET) has reduced sensitivity and increased cases of leakage. For example, in digital electronics, transistors are usually used to control the flow of current in an integrated circuit. This is important as it allows for the switching or amplification of the signals. Generally, many contemporary biosensors are currently mostly being fabricated using carbon based materials like grapheme with detection limits at pico-molar levels.

On the other hand, carbon nanoparticles are used to enhance sensitivity for due to increase active area for analyte to react in biosensor applications. Lastly, conducting polymer (CPs) are also important materials widely used in the construction of electrochemical biosensors. Currently, there are several types of conductive polymers used in biosensor applications some of which include PPY and polyaniline. For example PPY and polyaniline are mostly preferred due to their diverse electrochemical activities, compatibility with aqueous environments and ability to form various nanostructures like natotubes and nanowires.

1.2 Conducting Polymers

The conducting polymers are organic compounds that have the intrinsic ability to conduct electricity. These organic polymers can either have the metallic conductivity or semi conduction ability. These include PPY, polythiophene (PT), polyaniline (PANI), polycarbazole, polyphenylene, vinylene, PEDOT-polyethylene dioxythiophene [12, 13]. Figure 2 shows the structures of various neutral or undoped conducting polymers such as polyacetylenes (PA), PANI, PT, polyparaphenylene, PPY and polyphenylenevinylene [14]. The main advantage of these conducting polymers is their ability of dispersion processing. The conducting polymers are not thermoplastics. However, they are organic materials with similar qualities to those of insulating polymers [15]. They can provide high conductivity, although they do not have similar mechanical properties to other commercial polymers. Through the organic synthesis and dispersion techniques, the electrical properties of conducting polymers can be modified to perform various functions.

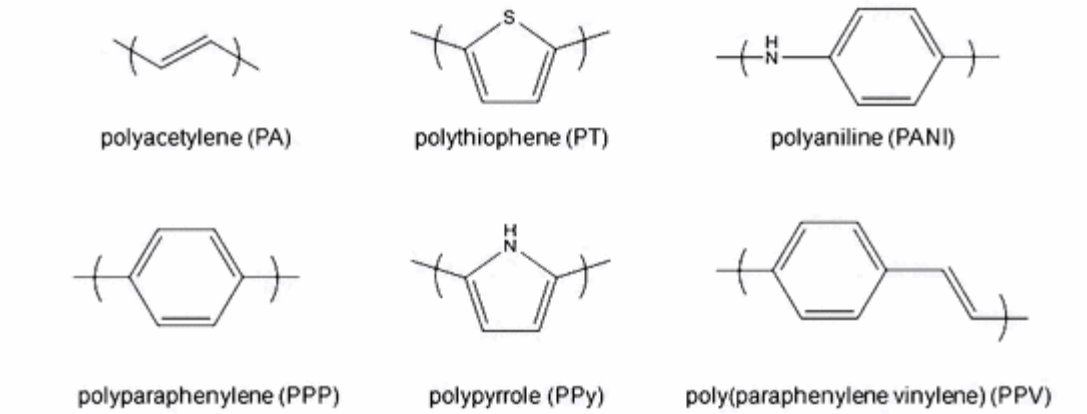

Figure 2. Chemical structure of pristine form of conducting polymers (reproduced with permission from Springer on Oct 21st, 2016) [12].

PPY is organic polymer that is formed through the polymerization of pyrrole. It is a yellow substance, which turns dark when exposed to oxygen. Although the PPY films are insoluble in solvents, they are swellable. Used as an insulator, the PPY becomes a good conductor of electricity when oxidized. The neutral and oxidized PPY can be seen in figure 3 [16]. The conductivity depends types of dopants and oxidation level in of the conducting polymer. The PPY can be doped upto 33% whereas PANI is doped for 50%. Polythiophene is a conducting polymer created through the polymerization of thiophene. They exist as semiconductor but can conduct electricity after doping or oxidation.

Lastly, PANI can be classified to semi-flexible rod polymer and it is also in the aromatic based polymer. . The compound was discovered more than one and half centuries ago only to attract the scientists' attention in the early 1980's. Polyphenylene vinylene or PPV is another conducting polymer that belongs to the rigid-rod polymer family. In this context, the compound's properties allow it to become a highly crystalline thin film that conducts electricity after doping. On the other hand, PEDOT is a conducting polymer, which is often used in the manufacturing of solar cells and LCDs among other things [4].

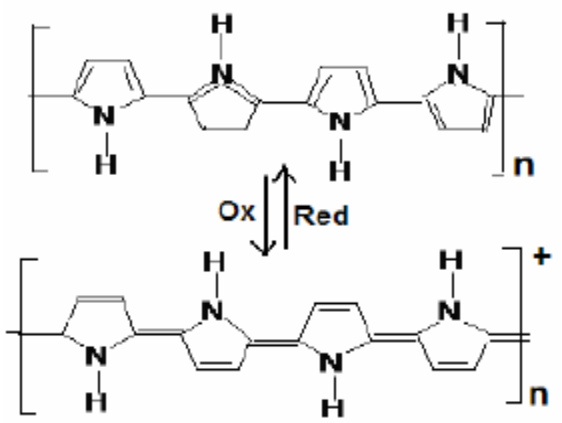

Figure 3. Various oxidized and reduced states of PPY (reproduced with permission from International Journal of ChemTech Research) [16].

1.3 Dichalcogenide Materials

The di-chalcogenide materials are monolayers and thing semiconductors consisting of transition metals. The discovery of graphene contributed to the discovery of the d-chalcogenide materials and their se in electrochemistry. They include MoS_2 [17], $MoSe_2$ [18], and FeS_2 [19] among others. MoS_2 is inorganic compound that is not affected by oxygen and acids. It is an indirect bandgap semiconductor used in electrochemical field. Molybdenum diselenide or $MoSe_2$ is another inorganic compound of the same family used as a semiconductor in electrochemical field. Others include FeS_2 and WeS_2 with a direct bandgap, which is essential in producing transistors and sensors in electronics industry [17].

This group of semiconductors has the capacity of absorbing photons with energy equals to or larger than that of their bandgap. This implies that they can absorb light with shorter wavelengths. As a result, they are effective emitters with the direct bandgap. Another feature that makes them perfect emitters is that they are monolayer materials. This explains why the atomic layer of MoS_2 is used to manufacture a phototransistor and other ultrasensitive detectors, which are important electronic devices [17]. Compared to graphene, these monolayer materials can be strained further. As a physical property of di-chalcogenide materials, the aspect of strain is directly proportional to

the bandgap. The indirect bandgap of the material will increase faster with an increase in strain levels. As a result, the emitting effectiveness of the materials is expected to reduce under high strain. This property allows for the mechanical tuning of physical electronic components. It gives the di-chalcogenide materials ability to be manipulated both electrically and physically [17].

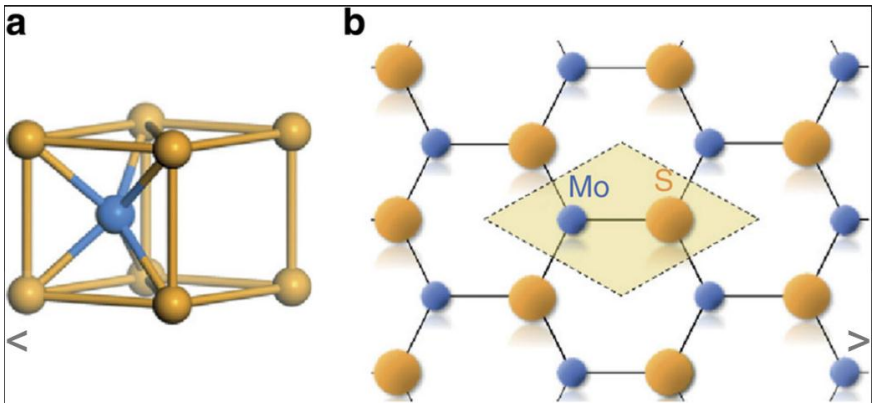

Figure 4. MoS_2 structure (reproduced with permission from Nature on Oct 23rd, 2016).

1.4 Composite Materials

A composite material refers to a material that is made from the combination of two or more constituent materials that have considerable distinct chemical and physical properties. The material produced has different characteristics from the individual constituents [20]. A composite material is formed when two distinct materials are combined to generate a unique and superior material. The modern composite materials are light and strong hence helps in more fuel savings and enhanced acceleration. The composites provide design flexibility since numerous of them can be molded into multifaceted shapes.

For example, the PPY is a conductive electro-active polymer that possesses some distinctive electrochemical and chemical properties. It is an electrically conducting polymer owing to its relative ease of synthesis [20]. The PPY composite film has been fabricated to understand the anion and cation exchange properties [21]. The PPY/palladium electrochemical film deposited on glassy carbon for electrocatalytic hydrogenation of 4-chlorophenol [22]. The PPY composite films

were made with polyaniline [23], polyethylene oxide [24], titanium-silica [25], carbon nanotube [26], graphite powder [27], hyaluronic acid [28], manganese dioxide [29] etc. The PPY displays high air stability and good electrical conductivity. It is composite material of significance due to its extensive array of technological applications in numerous areas that include electrochromic display devices, secondary batteries, sensor, capacitors, membranes and enzyme electrodes, and light-emitting diodes. The PPY can be obtained in bulk as fine powders utilizing the monomer's oxidative polymerization through the chosen transition ions metal in water and other numerous other solvents. The reaction between the pyrrole and aqueous ferric chloride is quick. The product is a black powder that is not soluble in all common solvents [20]. The salts of Iron (III) offer an appropriate means for oxidative polymerizing pyrrole and integrating their anions as the dopant ions.

On the other hand, graphene conducting polymer has a superior electrical conductivity that results in the conductive polymer when it fills the insulating polymer matrix. It has high charge mobility, high thermal conductivity. The mechanical, electronic and thermal properties of graphene rely on its monolayer, bilayer, and trilayer [30]. The graphene conducting polymer composites display enhanced mechanical strength and electrical conductivity minimizing the shrinking or swelling of conducting polymer, lengthening the life cycles and enhancing the charge storage capabilities.

The mixture of magnetic nanoparticles with the conducting polymer results in a ferromagnetic conducting polymer composite material that possesses a distinctive combination of both magnetic and electrical properties. It is evident in the electro-magnetic interference shielding applications [30]. The combination of the graphene with the conducting polymers depicts good electrical and thermal properties as the electronic conduction takes place at long range.

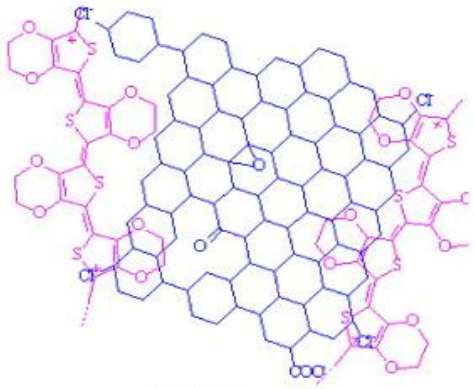

Figure 5. Composite conducting polymer-graphene structure (with permission) [31].

Similarly, nanodiamonds are the diamonds with a size underneath one micrometer. The production of nanodiamonds involves the impact events, for instance, the explosion impacts. The nanodiamonds are less prone to increase polymer viscosity. They do not form bundles or stacks; therefore, they can be dispersed in the matrix as compared to the 1D and 2D nanoparticles. A pure nanodiamond can be made through the detonation of a diamond blend and then formed through chemical purification [20]. Nanodiamonds conducting have a rounded shape, an active surface, and a diamond-like hardness and wear resistance. The spherical shape of nanodiamond makes the best use of the interphase volume per nanoparticle volume; thus, it contributes to enhanced mechanical properties of the composite.

Figure 5 shows the structure composite structure of polyethylene dioxythiophene-graphehe conducting polymer. (with permission) [31]. The nanodiamond particles in the polymer composites have a diamond structure that offers electrical resistivity and high thermal conductivity, superior Young's modulus, low coefficient of friction, hardness, biocompatibility and chemical stability. The small and uniform magnitude of nanodiamond conducting eliminates that necessity for expensive fractionation procedures that are needed for certain nanoparticles [20]. The nanodiamond has large and accessible external surface that helps in the maximization of the

interactions with the matrix, that is, the interphase volume. Moreover, it has tailorable and a rich surface that provides great flexibility for the rational design of the nanodiamond matrix interface. The nanodiamonds have been utilized as light beacons for chemotherapy and as a polishing material, lubricants for metal and additives to engine oil.

MoS_2 is an organic compound made of two elements only. These are molybdenum and sulfur. The compound is found naturally existing in a mineral in a silvery black ore called molybdenite. It is relatively less reactive and does not react with diluted acids and oxygen [32]. Its feel and physical appearance is analogous to that of graphite. Since it is a semi-conductor compound with an indirect bandgap of approximately 1.20 eV, MoS_2 has attracted attention of researcher on the electrochemical field. In the context of photonics and photovoltaics, MoS_2 possesses electric conductivity ability and it can emit light. These properties of MoS_2 open ways for its use and applications in various areas such as photodetectors, microelectronics and sensor applications[33]

On the other hand, PPY is an organic polymer, which is formed through the polymerization of pyrrole. There are various types of PPY, which include polythiophene, polyacetylene, and polyaniline. All these are conducting polymers and they have attracted attention of electrochemical researchers because of their ability to conduct electricity [33]. PPY are quasi-unidimensional as well as on-dimensional because of the presence of crosslinks and chain hoping in the polymers. Both unlopped and doped films of PPY do not dissolve in solvents, although they can be made to swell. Doping makes it to become brittle materials and they attain stability at from the atmospheric temperature to about 150^0C upon which the dopant begins to evolve [32].

1.5 Lactate Biosensor

Lactate sensor is one of the most modern biosensors, which have been created to facilitate the development of modern, fast biosensors. Generally, Lactate is one of the most critically important

metabolites that is usually formed as result of the anaerobic metabolism of glucose in the muscles of the body. Within the last few decades, various techniques have been used to sense the production of lactate due to its critical relevance in a wide range of fields including sports, clinical care and food processing among others. Currently one of the most popular electrochemical lactate biosensors is Amperometric enzyme biosensors which generally work by measuring the magnitude of current between reference and working electrodes. Currently one of the most popular electrochemical lactate biosensors is Amperometric enzyme biosensors which generally work by measuring the magnitude of current between reference and working electrodes.

The clinical samples and food processing industries have adoped to test the lactic acid in their samples. The research aimed at designing and developing lactate biosensors is no longer a new thing. Lactate biosensors have different analytical features based on sensitivity, fabrication, detection limit and linearity among others such as response time and ability of storage. There are two types of lactate biosensors, first one is based on the lactate oxidase (LOD) and another is based on lactate dehydrogenase (LDH) [3]. The lactate biosensors enhance optical sensing techniques, which has exhibited several advantages over the traditional electrochemical based techniques. Figure 6 shows the reaction involved in lactate oxide sensor [34]. These optical systems depend on photon transfer and detection. Table 2 reveals the properties of various conducting polymer based lactate sensor as studied [34].

So, we have attempted to make lactate biosensor on MoS_2-PPY based matrix using the lactate oxidase.

$$\text{L-lactate} + O_2 \xrightarrow[\text{oxidase}]{\text{L-Lactate}} \text{Pyruvate} + H_2O_2$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

Figure 6. Electrochemical reactions involved in LOD biosensors (reproduced with permission)[34].

1.6 PPY-MoS_2 Based Biosensor

Recently two-dimensional (2D) layered nano-materials like MoS_2[35] have recently drawn significant interest regarding their potential use as biosensors due their unique physicochemical properties associated with their quantum size and their ultra-thin structure[36]. MoS_2 used as a bio-sensing material has better sensitivity than graphene [6]. The use of MoS_2 brings the advantage of better sensitivity at a cheaper cost compared to the previous bio-sensing elements [37]. The MoS_2 can be synthesized using comparatively cheaper and economical methods including hydrothermal and solvent-thermal synthesis processes [38].

For example, 2D MoS_2 belongs to one of the most stable classes of inorganic graphene analogs that possess an intrinsic finite bandgap that are particularly suitable in use in electronics, optoelectronics as well as a diverse range of biosensor applications [39]. With a bandgap of 1.8 eV, conduction through MoS_2 can effectively be turned through between on and off states[40]. This is a critical property that is lacking in graphene and is important in diverse bio sensing applications. In addition, the presence of a bandgap ensures that MoS_2 has a high thermal and chemical stability. This is particularly owing to the nonexistence of the dangling bonds. The unique property makes MoS_2-PPY films to be excellent film for transistors with relatively low degree of power dissipation which are suitable for biosensor applications.

The high thermal stability is also critically essential in helping in the creation of high performance nano-electric devices like field effect transistors (FETs). These are used as ultrasensitive biosensors used for diverse clinically-relevant proteins as well as other biomolecules [41]. Although these biosensors are currently mostly being fabricated using carbon based materials like grapheme and nanotubes [42] with detection limits at pico-molar levels, the bandgap of MoS_2-ensures lower concentration detections.

Table 2. Properties of different conducting polymer based lactate biosensors(reproduced with permission) [34].

Enzyme; origin; amount used	Immobilization matrix; working electrode material	Type of transducer; immobilization method	Sensitivity	Detection limit	Linearity
D-LDH (EC 1.1.1.28); *Leuconostoc mesenteroides ssp. cremoris*; 23–187 U mg^{-1}	PEI/NAD^{+3}/carbon paste electrode	Amperometric; NR	NR	30 mmol L^{-1}	0.05–5 mmol L^{-1}
L-LDH (EC 1.1.1.27); rabbit muscle; 16–80 U mg^{-1} Glutamic pyruvic transaminase (GPT) (EC 2.6.1.2); pig heart; 0–5 U mg^{-1}	PPD film/carbon paste electrode	Amperometric, NR	0.56–1.1 mA $Mmol^{-1}$ L	0.03–0.6 mmol L^{-1}	0.5–77 μmmol L^{-1}/0.5–8.5 μmmol L^{-1}
LOD (no EC given); *Pediococcus sp.*; NR	Polyanion doped PPY film/Pt electrode	Amperometric, NR	5 μA $mmol^{-1}$ L cm^{-2}	5 mmol L^{-1}	0–2/0/16/0–30 mmol L^{-1}
L-LDH (EC 1.1.1.27); rabbit muscle; 1–4.5 U LOD (EC 1.1.3.2); *Pediococcus sp.*; 0.1–0.8 U	PANI/ITO coated glass plate	Amperometric, adsorption	5.5–38.5 μA $mmol^{-1}$ L	5×10^{-5} M	0.1-1to 1–4 mmol L^{-1}
L-LDH (EC 1.1.1.27); rabbit muscle; 0.1 mg	PPY–PVS/NR	Amperometric, cross-linking with glutaraldehyde	NR	NR	0.5–6 mmol L^{-1}
L-LDH (EC 1.1.1.27); rabbit muscle; 4.5 U LOD (EC 1.1.3.2); *Pediococcus sp.*; 0.1 U	PANI film/ ITO coated glass plate	Amperometric, adsorption	NR	0.05–1 mmol L^{-1}	0.1–1 to 1–4 mmol L^{-1}
L-LDH (EC 1.1.1.27); *Bacillus Stearothermophilus*.; NR	PANI–PAA/GCE	Amperometric; NR	NR	NR	0.4–0.55 mol L^{-1}
LDH (no EC given); NR; NR	MWCNT/ P3 MT polymer/ GCE	Amperometric, NR	NR	5.6×10^{-7} M	1.0×10^{-6}–5.0×10^{-4} M
L-LDH (no EC given); rabbit muscle;811 U/mg	pTTCA/MWCNT composite film/Au electrode	Amperometric, covalent	0.0106	1	5–90

NAD: nicotinamide adenine dinucleotide.
PPD: Poly-(o-phenylenediamine).
PANI/ITO: Polyaniline.
PPY–PVS: Polypyrrole–Polyvinylsulphonate.
P3 MT: Poly (3-methylthiophene).
PAA: Polyacrylate.
pTTCA: Poly-5,2′-5′,2″-terthiophene-3′-carboxylic acid.

In contrast, the sensitivity of graphene FET biosensors is usually constrained by the graphene's zero band gap and this often result in reduced sensitivity and increased cases of leakage [43, 44]. For example, in digital electronics, transistors are usually used to control the flow of current in an integrated circuit in order to permit for the switching or amplification. However, in the biosensing, there exist no physical gate and the binding amongst the receptor molecules that are embedded and the charged target molecules. On the other hand, two-dimensional MoS_2 are also suitable for biosensor applications owing to their good water solubility as well as their ability to obtain high fluorescence quenching efficiency within a relatively short time of about 5 minutes.

The molybdenum sulfide (MoS_2) is a scientifically and technologically important material. The potential applications of molybdenum sulfide are in electrochemistry [45], catalysis [46], lubrication [47] and a host material for intercalation chemistry has led to a growing interest in the sulfide synthesis. At present, the controlled fabrication or synthesis of structurally anisotropic molybdenum sulfide is of main significance in the heterogeneous catalysis because the surface property and the magnitude of the particles are of the key parameters to get extremely catalysts that are active and selective. Finally, molybdenum sulfide is a valuable material for numerous applications wherein high temperatures and dynamic pressures are involved [47]. It displays exceptional shock-absorbing or antishock property beneath extremely high shock wave pressures of approximately 25 gegapascel (GPa) that go along with concurrent high temperatures up to one thousand Celsius degrees.

The most interesting aspect of PPY is that that its oxidation enhances its ability to be an electric conductor. The polymer conductivity is based on conditions as well as reagents used during the oxidation process [48]. When the oxidation produces larger ions, the conductivity goes up. The polymer swells to compensate the ions in the doping process. It is the conductivity aspect of PPY

that makes it an interesting organic compound in use together with the MoS_2 to create sensors [49]. In the previous research on the same context, scientists have been concentrating on nanotube sensors. Although the carbon nanotube sensors have been exhibiting positive responses, they are not as selective as expected unless their functionality is enhanced by other chemicals, which makes the process more complex with expensive manufacturing process. MoS_2 made sensors have potential for excellence because of their high responsive nature and selectivity levels.

We have attempted to synthesize MoS_2-PPY composite film for lactate sensor application. The composite films were synthesized using the electrochemical technique by varying the current density in the electrochemical cell containing pyrrole monomer, dispersed MoS_2 and para-toluene sulfonic acid. The enzyme (lactate oxidase) was physically immobilized in nanocomposite film. The chronoamperometric technique was used for understanding the lactate sensor using MoS_2-PPY-lactate oxidase electrode. Various concentration of lactate was used to plot the lactate calibration curve.

CHAPTER 2. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

2.1 Electrochemical Synthesis of MoS_2-PPY Composite Films

MoS_2-PPY was electrochemically synthesized in three electrodes based electrochemical cell. The indium tin oxide (ITO) coated glass plate worked as working electrode, platinum as counter and Ag/AgCl as reference in three electrode cell. Various current densities were applied from electrochemical interface (potentiostat/galvanostat) to deposit MoS_2-PPY composite films from 30 second to 10 minutes.

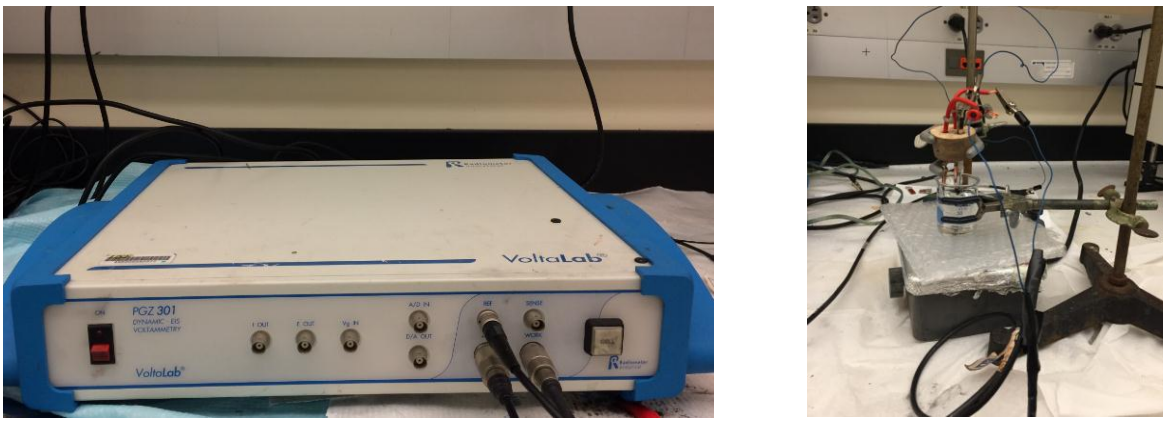

Figure 7. VoltaLab (left) and three electrodes set up to deposit the film (right).

2.2 Characterization

2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurement technique has been used to understand the chemical bonds in materials generally from 400 to 7000 cm^{-1} wavenumber [50]. The wave number is related to either absorption, transmission peak of the material. However, both qualitative and quantitative information of the chemical bonds can be determined using FTIR spectroscopic technique. The peak and the size of

chemical bonds determine the chemical structure and the amount of material present in the sample. Perkin Elmer Spectrum We have used One FTIR spectrometer to measure both transmission and reflection of samples for MoS_2-PPY and MoS_2-PPY-lactate oxidase samples. Figure (8) shows the FTIR spectrometer used to measure composite and enzyme immobilized films.

Figure 8. FTIR spectrometer.

2.2.2 Scanning Electron Microscopy (SEM)

The surface morphology and structural properties can be known by SEM technique. This is achievable through the use of field emission SEM tools. The SEM (scanning electron microscopy) machine takes the images which are then analyzed to determine the structural properties of MoS_2. It has been found that the MoS_2 nanosheets have a width between 10 and 15 nanometers [51]. SEM shows 3-D image because of the large depth of field. The magnification depth in SEM approaces to 10^4 [52]. The core working funtion of SEM is the focused electron beam and scanning the surface of the sample. The figure below is shown as a Ultra-high Resolution device.

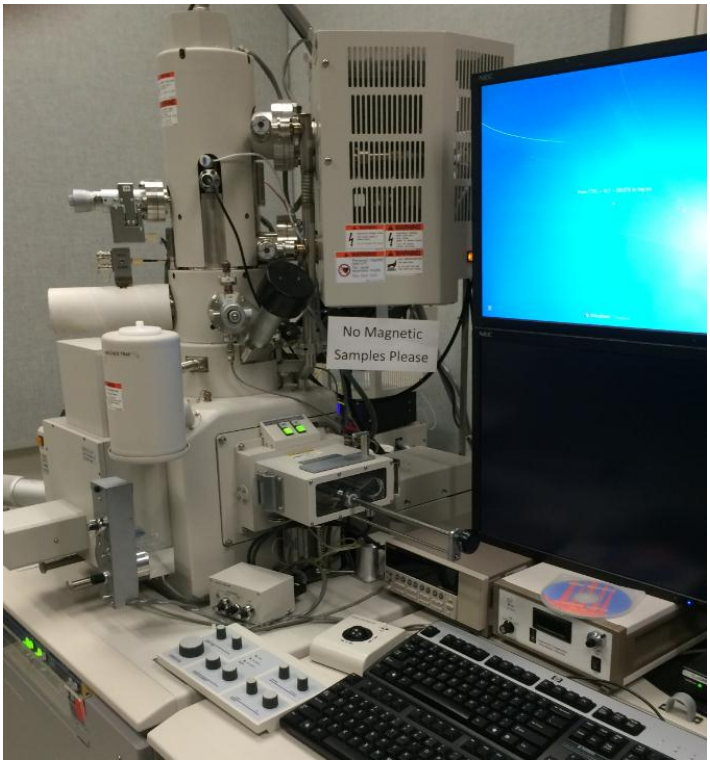

Figure 9. SU70 Hitcha scanning electron microscope instrument.

2.2.3 X-Ray Diffraction (XRD)

X-ray diffraction method is used to understand the crystallinity of material. The X-ray scan is done at different angular orientations and a specified scan rate [53]. The results are then interpreted. The X-ray diffraction tests that have been done on MoS_2 have confirmed the crystallinity of the nanosheets. The sheets are observed to be polycrystalline with hexagonal structures. The measurement of energy dispersive X-ray confirms the chemical properties of MoS_2. Experimental results have established that the crystals that were formed were MoS_2 [54]. Analytical instrument for XRD was used shown in figure below.

Figure 10. XRD instrument-Analytical X'Pert.

Using Bragg law can calculate and analyze the angles for coherent and incoherent scattering from a crystal lattice, Bragg law is:

$$2d \sin\theta = n\lambda_0$$

where: d=lattice interplanar spacing of the crystal

θ=X-ray incidence angle (Bragg angle)

λ=wavelength of the characteristic x-rays

2.2.4 UV-Spectroscopy (UV-Vis)

The other spectroscopy that is used to investigate the properties of the molybdenum nanosheets is the UV-vis spectroscopy. The technology tests the ultraviolet absorption properties of molybdenum disulfide. This photometric test exposes the sheets to UV spectrum at different levels. The testing machine captures the images that are subsequently analyzed for the absorption rates [55]. The UV absorption is used to determine the rate of conductivity. The sensitivity of

biosensor is also related to the conductivity of the immobilized matrix [56]. The degree of sensitivity is indirectly proportional to the level of current leakage [57]. Therefore this test can be used to gauge the band gap property of molybdenum disulfide. The instrument of UV-vis is called V530 Jasco Spectroscopy shows in the figure 11. The Beer-Lambert law is shown below:

$$A=Log_{10}\ (I_0/I)=\varepsilon lc$$

where: A= the measured absorbance;

I_0/I = the intensity of the incident light at a given wavelength;

I = the transmitted intensity;

L= the path length through the sample;

c= the concentration of the absorbing species;

ε= a constant known as the molar absorptivity or extinction coefficient.

Figure 11. UV-vis spectrophotmeter.

2.2.5 Raman Spectroscopic

The Raman Spectroscopy is a mechanism utilized in the determination of the number of layers in the MoS_2 produced. The approach involves two methods of investigation which are interlayer and interlayer spectroscopy[58]. These two mechanisms are at different vibrational frequencies. The intra-layer looks at the sheet's chemical composition and their fingerprints. The interlayer

investigations look at the layers and their peaks at low frequencies. The plot depicts the layers at different shear levels and helps to determine the number of layers with high accuracy

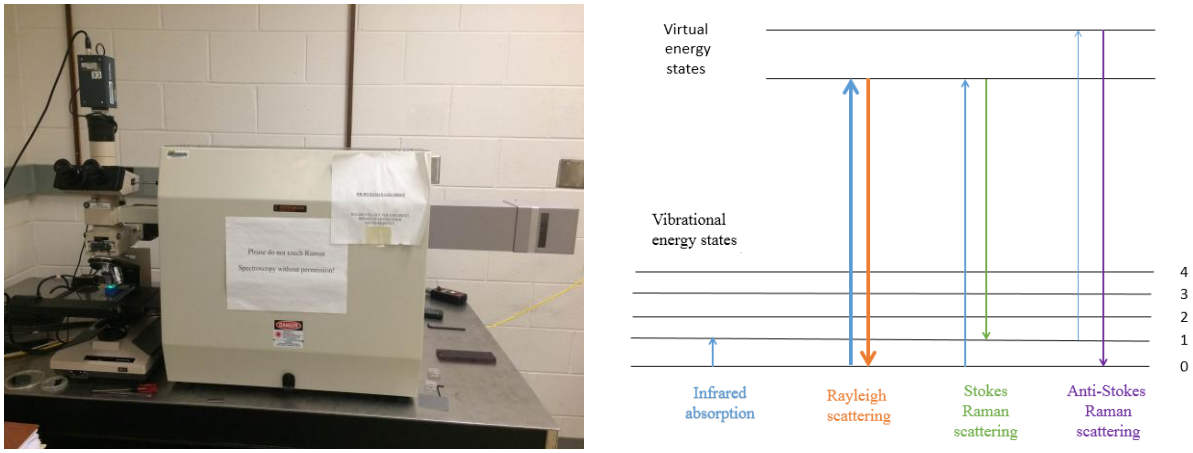

Figure 12. Raman spectrophotometer (left) and Raman band transition (right).

2.3 Biosensor Electrochemical Investigation

Electrochemical biosensors are important devices that particularly work by recognizing biological activity through identifying the electric signals of biological activities by transducers. Many of the biosensors are normally classified based on the transduction process or their recognition element. For instance, the two dimensional MoS_2-PPY films belong to one of the most stable classes of inorganic graphene analogs that possess an intrinsic finite bandgap that are particularly suitable in use in a diverse range of biosensor applications. Bio-sensing technology is very critical in the fields of chemistry, forensic investigation, and environmental sciences [59]. There are various biosensors that have been used in this field. For example, the relative efficacy of MoS_2 as a biosensor has resulted in a significant improvement in the bio-sensing world.

Electrochemically, MoS_2-PPY films possess a diverse range of electrical and chemical properties that particularly make them suitable for their bio-sensing applications in health, food processing, forensic and environmental protection industries. These unique properties have made

MoS_2-PPY film to be one of the most promising materials for biosensing technology. The key benefits of using MoS_2-PPY film in biosensing include high sensitivity, improved conductivity.

Firstly, one of the key electrical characteristics MoS_2-PPY films that make them best suited for their biosensing applications is the larger band gap of MoS_2 that ensures better electrical conductivity. Molybdenum has a wide band gap [60]. This quality is very important in the bio-sensing operation [61]. The wide band gap characteristic of MoS_2 permits current to flow while making it easy for the researchers to mitigate leakage. The net effect of this is an enhanced sensitivity and accurate readings [6]. This provides an edge over graphene as a bio-sensing material. Graphene has the disadvantage of zero band gap that eventually results in current leakage and reduced sensitivity.

Generally, semiconductor materials have band gap that can controllably be switched between different states such as conductive and insulated states. For example, with a bandgap of 1.8 eV, conduction through MoS_2 can effectively be turned through between on and off states. This is a critical property that is lacking in graphene and is important in diverse biosensing applications. In most cases, the larger the gap, the better the ability of a biosensing material to switch the states in order to effectively insulates any the leakage current. The wide band gap of MoS_2 not only enables the passage of current but also enhances the ability of MoS_2-PPY films to prevent current leakage thereby improving the accuracy and sensitivity of the readings.

On the other hand, the presence of a wider bandgap ensures that MoS_2 has a high thermal and chemical stability. This is particularly owing to the lack of the dangling bonds. The unique property makes MoS_2-PPY films has low degree of power dissipation which are suitable for biosensor applications. The high thermal stability is also critically essential in helping in the creation of high

performance nano-electric devices like field effect transistors (FETs). These can be used as ultrasensitive biosensors used for diverse clinically-relevant proteins as well as other biomolecules.

Although these biosensors are currently mostly being fabricated using carbon based materials like grapheme and nanotubes with detection limits at pico-molar levels, the bandgap of MoS_2 ensures lower concentration detections. On the other hand, the transduction technologies commonly used include field effect transistors (FETs), ion selective electrodes (ISEs) and gas-sensing electrodes among others. Chemically, MoS_2 semiconductor is 3 layered and is primarily formed by sulfur-molybdenum-sulfur bonds [62]. The atomic structure of the biosensor material consists of two hexagonal planes with each atom of molybdenum being covalently bonded to sulfur thereby forming a trigonal prism [63]. The electrochemical behavior of MoS_2 particularly depends on a number of factors. For example, MoS_2-PPY provides a sandwiched nanocomposite that can effectively be used as biosensors as they provide improved cycling stability and superior power density.

2.3.1 Cyclic Voltammetry (CV)

CV technique states an electrochemical technique which is used in measuring the current, with the application of potential in a electrochemical cell. It is done under the conditions with temperatures exceeding the one predicted in the Nernst Equation [64]. The CV is shown by cycling the potential between the working and counter electrode and the current is measured. The working potential is set in the electrochemical cell with respect to the working reference electrode at constant potential.

The process produces a resultant potential that consequently creates and excited signal shown in the figure one below. Based on the figure below, the resultant potential first produce a negative scan that starts from the highest potential at point a and ends at point d with lower potential [33].

The potential at the point d is called the switching potential. It has sufficiently enough voltage to cause either an oxidation or reduction on the analyte. When the reverse scan is done from d to g, a positive scan of potential energy occurs.

The figure (13) also indicates a specific reduction that takes place between a and d, and the oxidation that occurs between d and g. The cycle shown in the diagram can be repeated during the process.

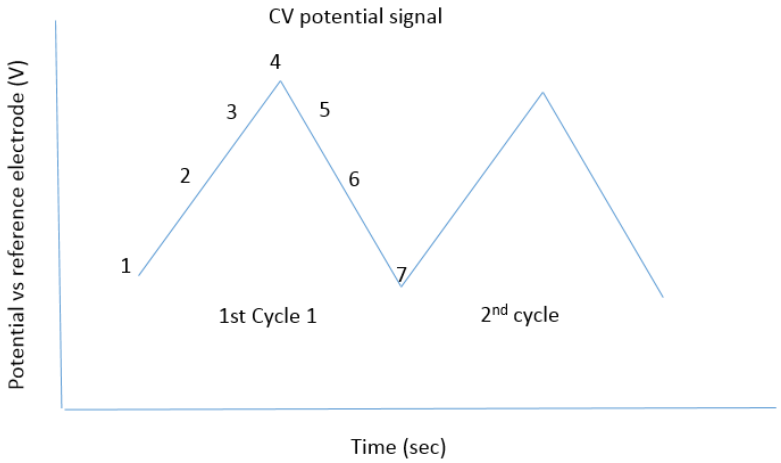

Figure 13. Excitation of signals during the CV.

During the potential scans, we can obtain a CV by measuring current of the working electrode**.** The CV machine involves electrochemical cell, potentiostat, galvanostat, current-to-voltage converter, and data acquisition system. The electrolysis cell is made up of the reference electrode, working electrode, electrolytic solution and counter electrode [65]. The working electrode potential value is directly proportional to time and shows linearly. The reference electrode does maintain the constant potential with respect to counter [33]. The electrolytic solution mainly supplies ions to the three electrodes throughout reduction and oxidation processes. The potentiostat refers to an electronic device that utilizes direct current power to generate potential energy. This energy can be maintained at an accurately determined value while small current is allowed to flow into the system without any change in voltage. Lastly, the current-to-voltage converter is used in

measuring the resultant current while the data acquisition system processes and produced the resultant voltammogram [66].

The CV is has several applications in electrochemical field. It is used in the qualitative study of information regarding electrochemical processes under different conditions. These include the existence intermediary chemicals and compounds during the oxidation-reduction reactions as well as the reversibility processes [67]. The CV is useful in determining the system's electron stoichiometry, diffusion coefficient and formal reduction potential, which is essential in application as an identification tool. The CV results have been investigated the doping behavior of MoS_2 and PPY. It helps to determining the concentration of unknown solutions by creating current vs. concentration curves [33].

Investigating of the electrochemical properties of molybdenum disulfide has been carried out. The properties to be measured are CV, galvanometric discharge test, and electrochemical impedance analysis. Three electrode test can be used in this investigation in which case the main electrode is MoS_2 while the reference electrode and counter electrode are saturated calomel electrode and platinum respectively. The solution that forms the electrolyte is phosphate (6.7mM aqueous solution).

With the set up in place, a potentiometer such as VoltaLab PGZ301 instrument can be used to measure the cyclic voltammetry of the MoS_2 against the reference electrode. The potentiometer window from -0.6 V to 4.0 V is scanned in various rates, for example, 5, 10, 20, 50, up to 100mV/s. The impedance testing is carried out using an impedance analyzer. The galvanometric discharge tests are carried out using a galvanometer.

There are various kinds of biosensors some of which may include electrochemical, calorimetric, optical and acoustic sensors. The first step in the experimentation process is the

preparation of the MoS_2 sheets. The MoS_2 nanosheets are prepared by hydrothermal processes at temperatures of 200 ℃ [68]. The two primary components that are reacted to produce MoS_2 are Thioacetamide [69] and Sodium Molybdate [70]. The second step in the nanosheets preparation is the landing surface. The place where the sheets are to be laid ought to be prepared. It is recommended that a stainless sheet is used for holding the MoS_2 produced. The stainless steel surface is polished and cleaned via ultrasonic means utilizing acetone and ethanol. The MoS_2 is then poured on the sheet and then left at 200 ℃ for 24 hours before being cooled to the room temperature. After cooling, the stainless steel sheet with the MoS_2 films is then cleaned and dried at a temperature of 50 ℃ in an oven. This process produces the nanosheets that can be used for further tests.

2.3.2 Electrochemical Impedance Spectroscopy

Resistance is a concept in electricity, which refers to the ability of elements in an electric circuit to resist the electric current flow [71]. According to the Ohm's, resistance (R) is the ratio amongst the current (I) and voltage (E), and it is expressed as follows:

$$R = E/I$$

Even though the above equation is popular in electrical study, its application is limited to a single element circuit with the ideal resistor. In this context, an ideal resistor exhibits three main properties. The first property is that it conforms to the Ohm's law at all currents and voltages. The second property is that the value of its resistance is not dependent of frequency. Lastly, the voltage signals and the AC current passing through the resistor are always in phase with one another. However, the idea of ideal resistance does not apply in the real world that contains more complex behavior of even a simple circuit [66].

Just like the resistance, the impedance measures the capability of circuit to fight or resist the electrical current flow. Nevertheless, impedance as compared to the resistance is not limited to the above stated three properties. It is because the concept of impedance is applied in real world problems. The electrochemical impedance is estimated by measuring the AC potential in a electrochemical cell. Afterward, the current through the cell is measured. For instance, by applying an AC potential excitation, we can analyze the current signal using Fourier series as the sinusoidal functions. In the case of electrochemical impedance, the measurement is done using a small excitation signal to attain a pseudo-linear response [33]. The current as well as potential is sinusoidal wave at similar frequency those with shifted shape as shown in the diagram below.

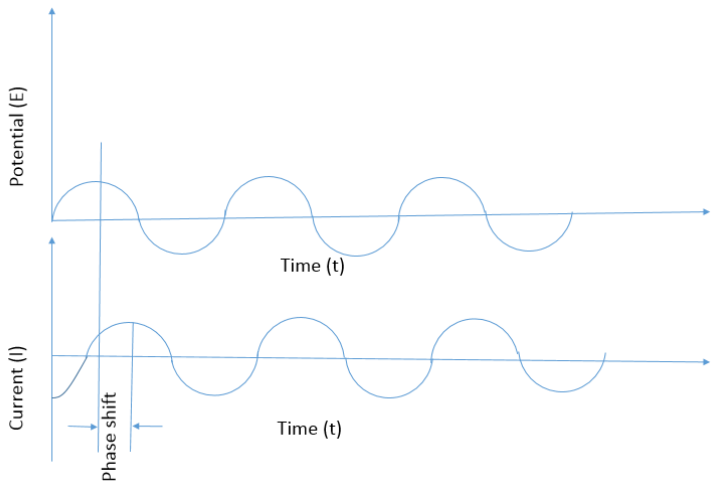

Figure 14. The Sinusoidal current and potential response in a linear system.

Being a concept used in analyzing real life behavior of electric components, impedance takes a transient response. In this case, the excitation signal used is expressed as shown in the following equation as a function of time:

$$E_t = E_0 \sin(\omega t)$$

In the above equation, potential energy at time is E_t, t, while E_0 is amplitude of the signal and *w* is the radial frequency of the signal [71]. The association among radial frequency ω and the normal frequency f are shown in following equation:

$$\Omega = 2\,\pi\,f$$

In a circuit system which is linear has the response of the signal I_t with phased shift angle Φ and amplitude current of I_0.

$$I_t = I_0 \sin(\omega t + \Phi)$$

With the expression for the current and voltage signals shown above, we can develop the equation for impedance, which corresponds to the resistance as expressed in the Ohm's law as follows:

$$Z = \frac{E_t}{I_t} = \frac{E_0\ Sin(\omega t)}{I_{0Sin(\omega t+\ \Phi)}} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t+\Phi)}$$

From the expression in equation above, we can deduce that the phase shift angle and its magnitude of the impedance signal.

In electrochemistry system, we can still apply the same principles of electric circuits to analyze them. The theory of electrical circuit is applied based both on non-linear as well as linear systems. While analysis of the linear circuits tends to be direct, non-linear circuits are a bit complex. The resistance of solutions is a significant aspect of impedance in electrochemical cell [33]. The compensation for the solution resistance in the modern three electrode potentiostat occurs amongst the electrodes for reference and counter electrode. Nevertheless, any solution resistance in this case is considered when modelling the cell. The impedance of the ion solution relies on the ion's concentration, in the solution and other aspects such as the temperature and the type of ions. When a solution is placed in a bound region of area (A) and a uniform length (l) in which it carries a uniform current (A), then the resistance is defined as follows:

$$R = \rho \frac{l}{A}$$

In the above equation, is a constant called resistivity of the solution whose reciprocal (k = 1/p) is called conductivity and is mostly used in developing the association with its resistance as follows:

$$R = \frac{1}{k} \; x \; \frac{l}{A} => k = \frac{l}{RA}$$

The above equation is important in controlling conductivity of MoS_2 doped with PPY to make the lactate sensor [71]. The conductivity of the chemical determines how excellent it can be used as a sensor.

2.3.3 Chronoamperometry

Chronoamperometry is a technique in electrochemistry in which the working electrode potential is stepped and the resultant current caused by the stepping process is exhibited as a function of time. The values of the electrolyzed species are gotten through the ratio of the peak oxidation current and peak reduction current [72]. Nevertheless, Chronoamperometry is a pulsed technique that generates high amounts of charging currents and this current takes a transient form and decays exponentially with respect to time like any RC circuit. In many electrochemical cells such as those in MoS_2-PPY, this current decay is much slower compared to the charging decays. The Chronoamperometry is used to investigate electrochemical components with three electrode systems as discussed above. Because the integration of current occurs within a relatively longer time intervals, the use of Chronoamperometry helps in giving a better signal to noise ratio in close comparison to other techniques such as amperometric technique.

For instance, deoxygenation of dimethylformamide (DMF) in an Anthracene causes a reduction at the surface of electrode with a given value of negative potential. Such reduction processes are limited by diffusion, and subsequently causing the drop in current with time. By measuring the current i(t) at a fixed time denoted by τ, there does not exist any other moment of point current i(τ). At this point, a mass-transfer-limit area is reached and at this point, the anthracene used will arrive fast as possible to the electrode based on the diffusion gradient. This technique finds its application in several ways in the field of electrochemical [72].

It can be used to measure the concentration by measuring the current (I) against concentration at any fixed time (τ). The method can be used in analyzing the current-time curve shape to study the coupled chemical reactions such as in MoS_2-PPY. The importance of Chronoamperometry is that it acts as a fundamental technique on which other similar techniques draw their knowledge. Therefore, its use in the study of electrochemical signal is essential in assessing the conductivity level of organic compounds used in creating sensors and other applications.

CHAPTER 3. MOLYBDENUM DISULFIDE-PPY FILM

3.1 Synthesis

We have synthesized MoS_2-PPY composite film electrochemically. The MoS_2-PPY composite films were synthesized using the electrochemical technique by varying the current density in the electrochemical cell containing pyrrole monomer, colloidal MoS_2 and para-toluene sulfonic acid. The current density of 8 mA/cm^2 was applied for 30 seconds, 1, 2, 5 and 10 minutes to deposit different thicknesses of MoS_2-PPY composite film.

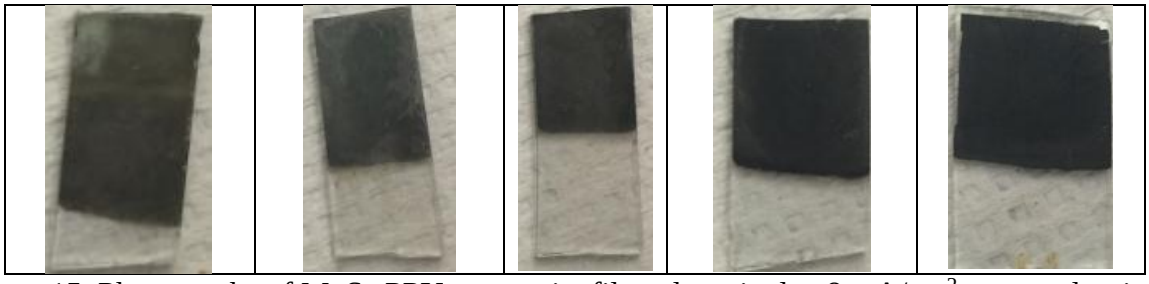

Figure 15. Photographs of MoS_2-PPY composite films deposited at 8 mA/cm^2 current density as a function of time (30 sec, 1 min, 2 min, 5 min and 10 min).

The MoS_2-PPY composite films were characterized by using SEM, X-ray diffraction, UV-vis, FTIR, Raman, CV and chronoamperometric techniques.

3.2 Characterization

3.2.1 FTIR Studies

The infrared (IR) measurement on PPY-MoS_2 using FTIR spectrophotometer is shown in figure 16. Fig. 16 (red line) displays infrared peaks at 540, 636, 712, 977, 1085, 1384, 1490, 1590 ,2378, 3628, 3738, and 3834 cm^{-1} for PPY-MoS_2 film of FTO glass substrates. The various IR band are given in Table 3.

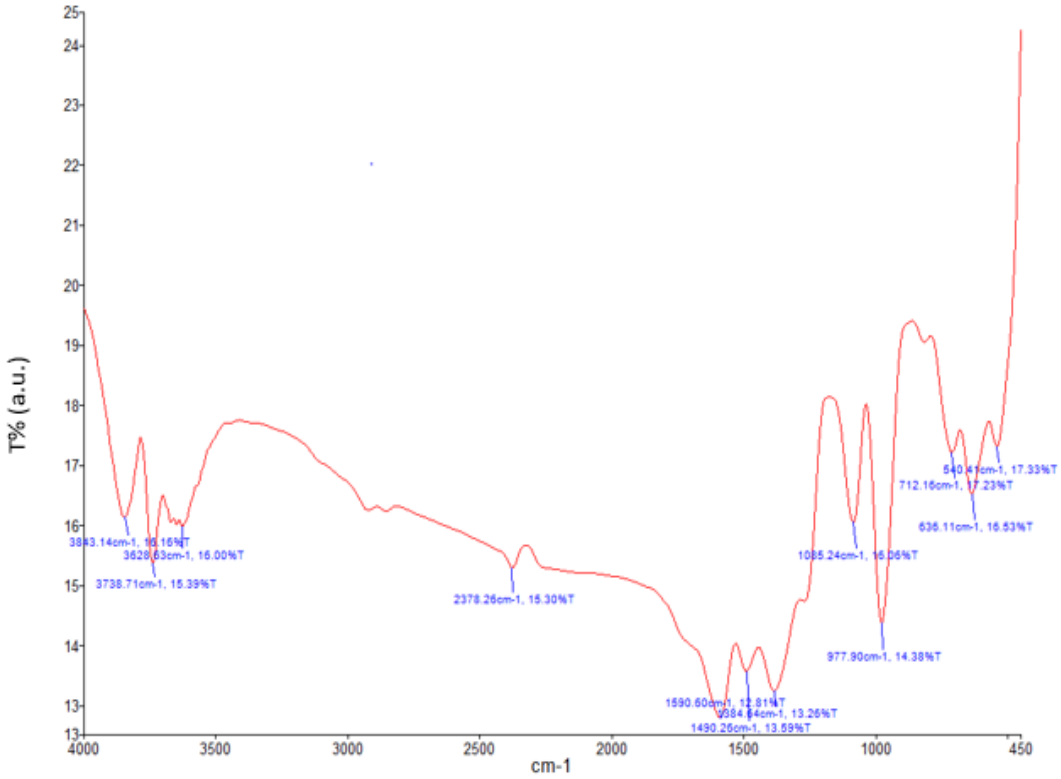

Figure 16. FTIR spectra of PPY-MoS_2.

Table 3. Characteristic infrared red bands of peaks of PPY-MoS_2 film.

cm^{-1}	PPY-MoS_2
C-H stretching	3834
O-H stretching	3738
N-H stretching	3628
PY ring	2378
C=C bending	1590
C-C and C-N bending	1490
Mixed bending with C-N and $-CH_3$ symmetric	1384
C-O and C-H vibration	1085
-OH, S-O	977
C-H	712
S-S	636
N-H wagging	540

3.2.2 SEM Studies

The morphology on the film was observed using SU70 Hitcha scanning electron microscope instrument. The operating is under 25 KV emission. Figure (17) shows SEM structure of PPY-MoS_2 film. SEM pictures show the typical granules structures of PPY film. However, MoS_2 nanomaterial is wrapped with the PPY to give the various sizes of granules.

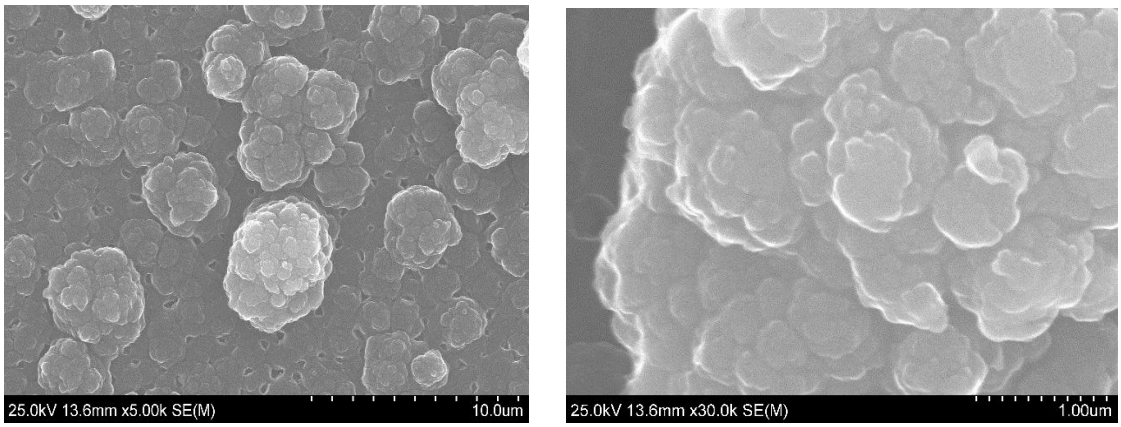

Figure 17. SEM images of PPY-MoS_2.

3.2.3 XRD Studies

XRD measurement of the PPY-MoS_2 film shows 2Θ peaks at 14.4°, 37.7° which perfect match with the MoS_2 peaks in figure 18. All the diffraction peaks can be assigned due to MoS_2. There is a low energy peak at peak 26.5 ٩n figure (18) PPY. According to the literature, the peak of the PPY should occurs at 25 °. The peak position has shifted compared to reported value of PPY film, which may result from the amorphous structure of PPY or due to MoS_2 doping in PPY film. There is no other crystalline forms which are found consistent with the result of the XRD pattern in figure (18).

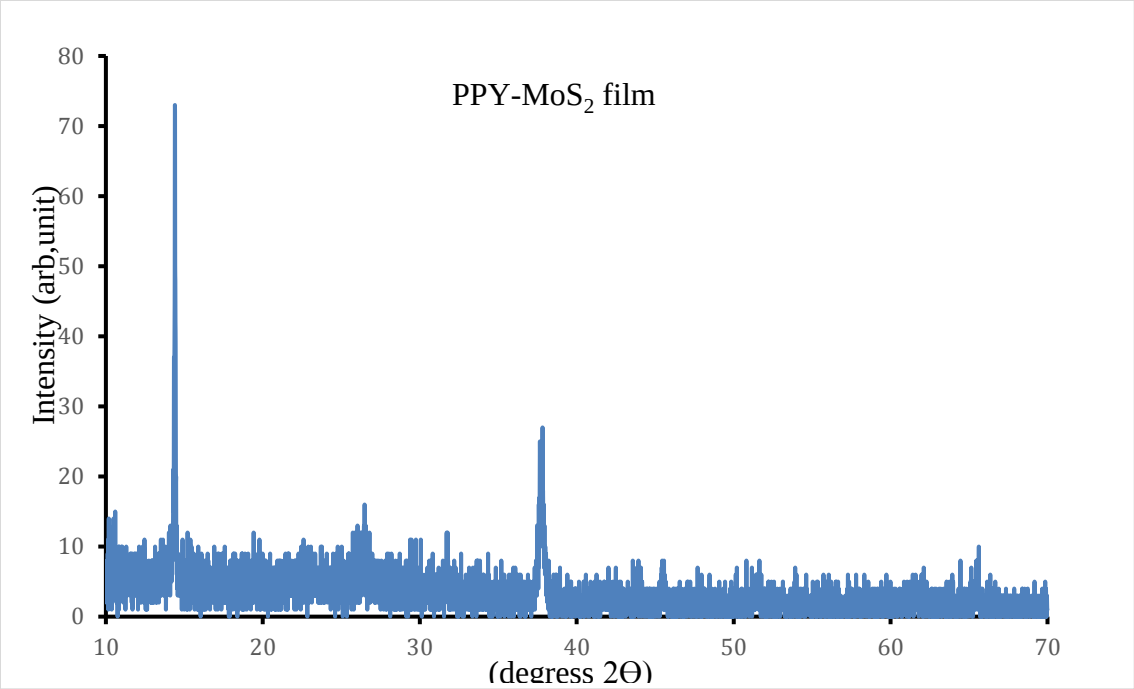

Figure 18. XRD measurement of the PPY-MoS_2 film.

3.2.4 UV-Spectroscopy

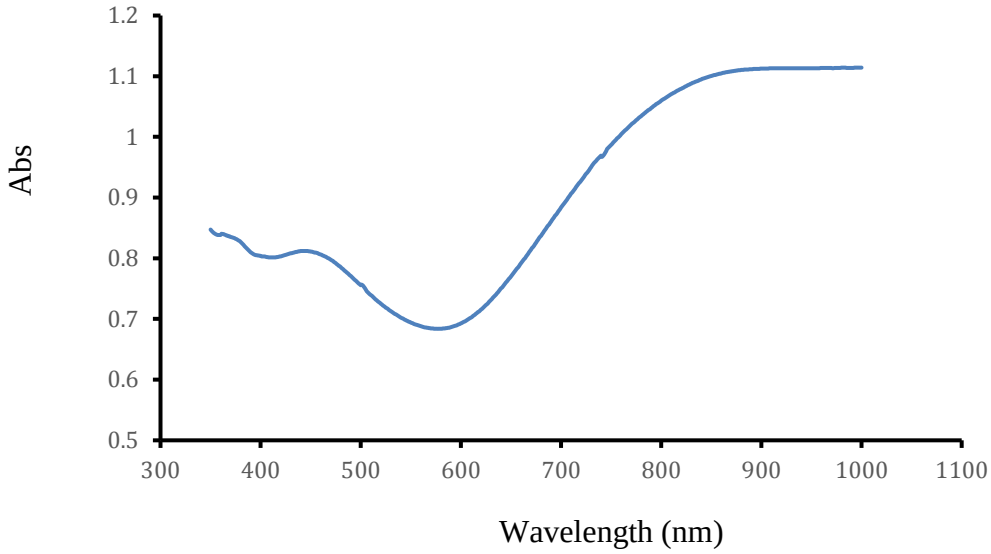

Figure 19. UV-vis for PPY-MoS_2 film.

The UV-vis measurement is used by Jasco V-530. Figure (19) shows the absorption peaks of PPY-MoS_2 film are at 380 nm, 454 nm and 873 nm. According to the Beer-Lambert's law, utilize

the peaks observed, the band gap of PPY-MoS_2 film is 1.8 eV, conduction through MoS_2 can effectively be turned through between on and off states of composite film.

3.2.5 Raman Studies

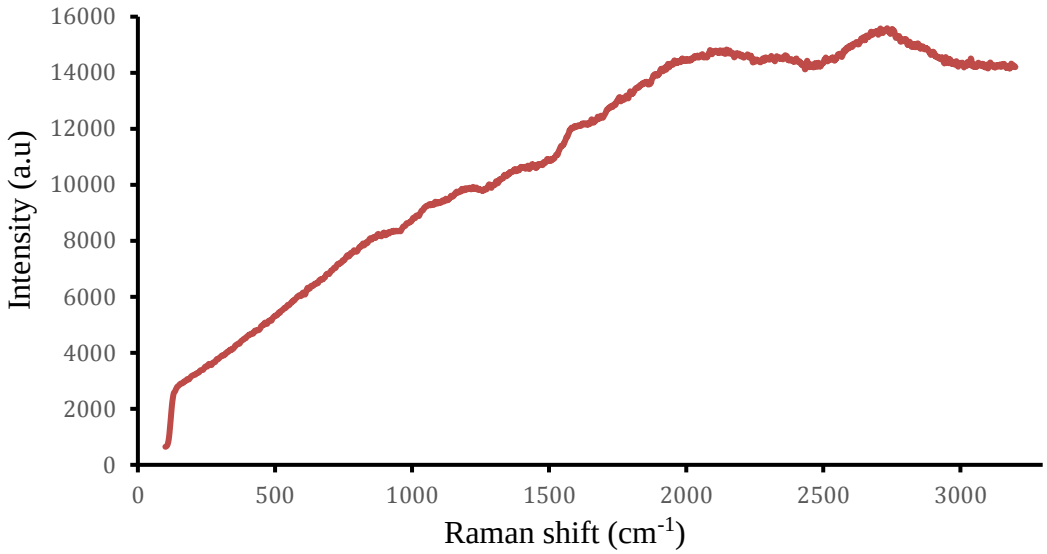

Figure 20. Raman spectra for PPY-MoS_2 film.

Raman spectrum of the PPY-MoS_2 film is shown in Figure (20). The two highest peaks which are appeared at 2095 cm^{-1} and 2748 cm^{-1}, respectively. The four weaker peaks appear at 888, 1074, 1390 and 1590 cm^{-1}. These peaks matched with PPY and MoS_2 materials separately. No other crystalline peaks are found matched with this Raman spectrum report.

3.3 Electrochemical Methods

3.3.1 CV Studies

One of the tests involves investigating the electrochemical properties of MoS_2. The properties to be gauged are CV, galvanometric discharge test, and electrochemical impedance analysis. Three electrode test can be used in this investigation in which case the main electrode is MoS_2 while the reference electrode and counter electrodes are saturated calomel electrode and platinum, respectively. The solution that forms the electrolyte is phosphate (6.7mM aqueous solution).

With the set up in place, a potentiometer such as VoltaLab PGZ301 instrument can be used to measure the CV of the MoS_2 against the reference electrode. The potentiometer window from -300mV to 800mV is scanned in various rates, for example, 5mV/s, 10mV/s, 20mV/s, 50mV/s, up to 100mV/s. The impedance testing is carried out using an impedance analyzer. The galvanometric discharge tests are carried out using a galvanometer.

The Figure (21) is the effect of PPY-MoS_2 film on the electric conductivity without the enzyme coated electrode was evaluated by CV studies under different scan rate from 5 to 100mV/s. The liquid solution is phosphate buffer (PH 7). The various color CV curves are shown in figure, there is no obvious peaks of oxidation or reduction. All the current difference caused by the voltage is changed.

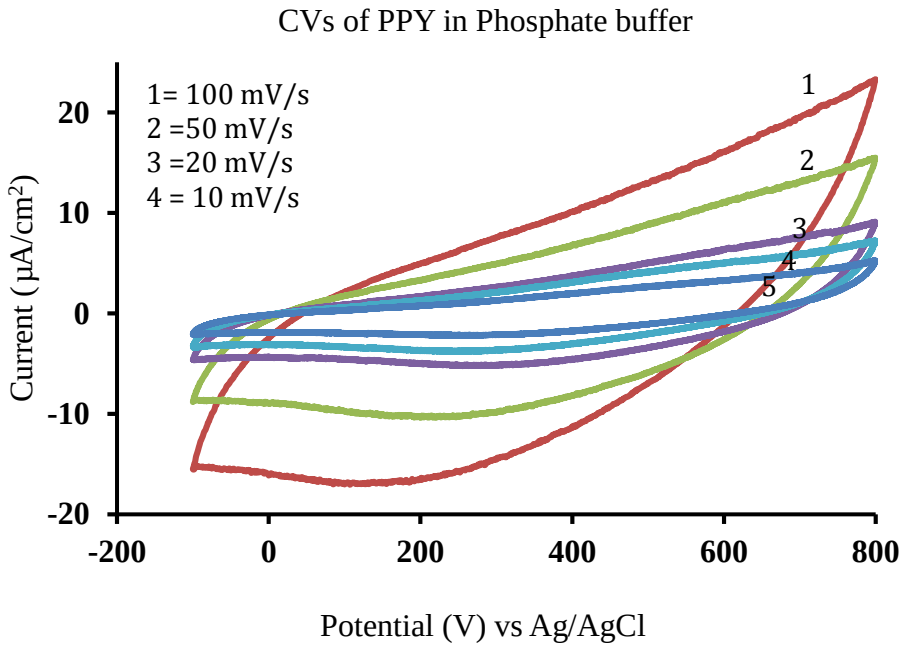

Figure 21. PPY-MoS_2 film in buffer 80ml 6.7mM phosphate buffer with different scan rate.

CHAPTER 4. EFFECTS OF DOPANT IN MOS_2-PPY FILM FOR LACTATE SENSOR APPLICATION

4.1 Introduction

MoS_2-PPY films are increasingly being utilized for an extensive array of biosensor applications that ranges from detection of biological activities to identification of electric signals that can be detected by transducers. This is particularly attributed to their two-dimensional structure and rich optical and electronic properties [73]. Bio-sensing technology is very critical in the fields of chemistry, forensic investigation, and environmental sciences. There are various biosensors that have been used in this field. The discovery of the efficacy of MoS_2 as a biosensor has brought a significant improvement in the bio-sensing world.

Dopant has a diverse number of effects on MoS_2-PPY film meant for lactate sensor application. In the manufacture of semiconductors like MoS_2-PPY films, a dopant is an important trace impurity element that is normally added in low concentrations to help alter the optical or electrical properties of the substance [74]. This is particularly because the crystalline nature of the atoms of a dopant which causes the electrical conductivity in a semiconductor. For example, MoS_2-PPY film for lactate sensor application is likely to act more like a conductor than like a semiconductor when a dopant is added. It is critically important to design friendly and stable interface among the underlying physicochemical transducer and the biorecognition membrane layer, for example, the metallic electrode. It assists in creating stable, effective and reproducible bio-transducers [75].

A biosensor is an important component of electrochemical development. It is composed of bio-receptor and a transducer. The bio-receptor component refers to the biomolecule that identifies the target analyte. Numerous previous researches have increasingly focused on ways developing ways of sensing the production of lactate due to its critical importance in clinical care, food processing and sport medicine. Generally, the seeding layer enhances the loaded enzyme activity. It offers a surface that enables an enzyme adsorption without the denaturation. For example, the PPY has a stabilizing influence on the enzymes. The seeding layer considerably reduces the average biofabrication time for the unseeded biotransducer and seeded biotransducer. It helps in improving the reproducibility in biofabrication

The discovery of graphene has developed interest among researchers in the context of layered materials, which include the transition metal dichalcogenites (TMD). The MoS_2 in a semiconducting material in the family of TMD and it is among the chemicals in this family with an outstanding chemical and thermal stability as well as high mobility [72]. It has arisen as one of the utmost encouraging candidates for electrochemical research and thus its uses in the development of sensors. Since MoS_2 relies on governing the position of the Fermi energy (E_f), besides its importance to comprehend the necessity of doping or gating. Also doping helps in creating a bandgap and determining the Fermi energy in MoS_2. The molybdenum sulfide (MoS_2) is a scientifically and technologically important material. The potential application of molybdenum sulfide in electrochemistry, catalysis, lubrication and a host material for intercalation chemistry has led to a growing interest in the synthesis of the sulfide [76].

The molybdenum sulfide surface is more covalent than an oxide surface. Thus, its electron donating and accepting properties are non-ideal [77]. The cyclic voltammograms of PPY films are mainly characterized by a well-defined redox process that corresponds to the oxidation and

reduction of the PPY backbone and a large capacitance effect that results from the redox process and the film's porous nature. The oxidized potential is sharper for the doped PPY films doped than the reduction potential. The oxidation of the film makes the layer situated next to the electrode surface to be oxidized first; thus, generating a conducting layer that facilitates the oxidation of the next layer until the conducting layer encompasses the entire film.

The ionic diffusion coefficient decreases with the reduction of the polymer. It is due to the ladder doped structure for the PPY films doped with polysulfonated aromatic compounds. The dopants serve as cross linkers at the positive positions alongside the neighboring oxidized PPY chains. The anions generate open channels within the polymer that are oxidized wherein the rapid ionic movement can take place [73]. The reduction of the polymer leads to free binding of the anions with the incoming cations triggering the open structure to collapse thereby hampering ionic movement. Consequently, there will be a decrease in the coefficient of ionic diffusion.

The (PANI) 0.35 MoS_2 and (polyethylene oxide) 0.92 MoS_2 composites show a p-type metallic conduct that may undergo a change to insulator at temperature between 14 K and 9 K. The PPY encapsulation amongst the molybdenum sulfide layers through an original position oxidative polymerization process has been understood clearly. The addition of polyethylene oxide and polyethylene glycol electrolytes considerably augments the process of nucleation and enhances the electrochemical and structural properties of the electrodeposited MoS_2 cathode in the three-dimensional Li-ion micro batteries.

The lactate oxidase (LOD) catalyzes lactic acid to pyruvate and hydrogen peroxide (H_2O_2) in the lactate oxidase centered amperometric biosensor. It can be oxidized at the electrode surface. The doping of the molybdenum sulfide monolayers with the rhenium and introducing the gold adatoms augment the local chemical affinity. The reaction of the top sulfur groups with the noble

metals has been utilized to attach the gold nanoparticles. Additionally, the nickel ions can be coordinated covalently-bound to the top sulfur layer of the nanoparticles of the molybdenum disulfide.

4.2 Effects of Doping

Doping particularly involves the introduction of impurities into a given semiconductor material in order to modify its electrical conductivity properties. The dopant is normally integrated into the structural lattice of the semiconductor crystals thereby affecting is electronic configuration[78]. As earlier been noted, doping normally result in a diverse number of effects on semiconductors like MoS_2-PPY films. For instance, a dopant is an important trace impurity element that is normally added in low concentrations to help alter the optical or electrical properties of the substance. The addition of a dopant can shift the Fermi levels contained within the material thereby resulting in a material with more p-type or n-type based on the nature of dopant. Generally, the bandgap of MoS_2 and its Fermi energy can be measured using both the scanning tunneling microscopy and scanning tunneling spectroscopy with the getting abilities. They can also be used to track its behavior and evolution of its gate voltage [72]. This way, the doping effects in it can be evaluated. In this context, the measured bandgap is compared to the position of the Fermi energy, which is often below the conduction band.

Subsequently, the measured bandgap is ~1.3eV and the position of E_f is ~0.35eV, which is underneath the conducting band and is consistent with the n-doping for the MoS_2. By using spectroscopy, the source of n-doping in MoS_2 can be traced in order to determine defects if any, which attribute to S vacancies. In the case of layered MoS_2-PPY, there is a high level of n-doping, which cannot be attributed to the S vacancies. From the observation, it can be deduced that n-doping of a thin-filmed layer sample occurs because of the charge traps at the interface of the

substrate[72]. Finally, doping elements can lead to a realized in MoS_2 properties through changing certain synthesis parameters.

4.3 Enzyme Immobilization

Enzyme immobilization on matrix. The enzyme can be immobilized on any matrix through self- assembly, adsorption technique, entrapment, affinity immobilization, covalent binding, Langmuir-Blodgett technique, electrochemical, layer-by-layer deposition, solution casting, dip technique etc. [79-83]. The enzyme immobilization is dependent on pH value of the enzymatic solution, temperature, buffers, reacting time constant, inhibitors etc. The controlled immobilization technique improves the stability of enzyme, reduces the enzyme inhibition and also increases the stability, sensitivity and selectivity in biosensor.

4.4 Characterization

4.4.1 FTIR

The infrared (IR) measurement on PPY-MoS_2 sample and PPY-MoS_2-enzymeenzyme samples were measured using FTIR spectrophotometer. FTIR spectra of the PPY-MoS_2 film, PPY-MoS_2-enzyme film and PPY-MoS_2-enzyme film used for lactic acid detection on FTO glass substrate are shown in Figure (22). Figure (22 red line) displays infrared peaks at 540, 636, 712, 977, 1085, 1384, 1490, 1590, 2378, 3628, 3738, and 3834 cm^{-1} for PPY-MoS_2 film of FTO substrates. Figure (22 green line) shows infrared peaks at 798, 960, 1056, 1244, 1574, 2491, 3627, 3739, and 3842 cm^{-1} for PPY-MoS_2-enzyme film of FTO substrates. Figure (22 blue line) observes infrared peaks at 606, 805, 955, 1060, 1238, 1319, 1572, 1725, 2105, 3628, 3737, and 3840 cm^{-1} for PPY-MoS_2-enzyme film reacted with lactic acid on FTO substrates. The peaks are obvious shifted when the lactate oxidase when coated on the film which means that the biochemical property of the PPY-MoS_2 film can be influenced by the enzyme. From the figure, the conductivity

appears more sensitive when the enzyme coated. However, the peaks between green curve and blue curve are almost same. There is no significant change after the PPY-MoS_2 film with enzyme reaction as a lactate biosensor which can be proved for PPY-MoS_2 film used for a lactate biosensor have a good stability. Multiple use is an important property for the biosensor.

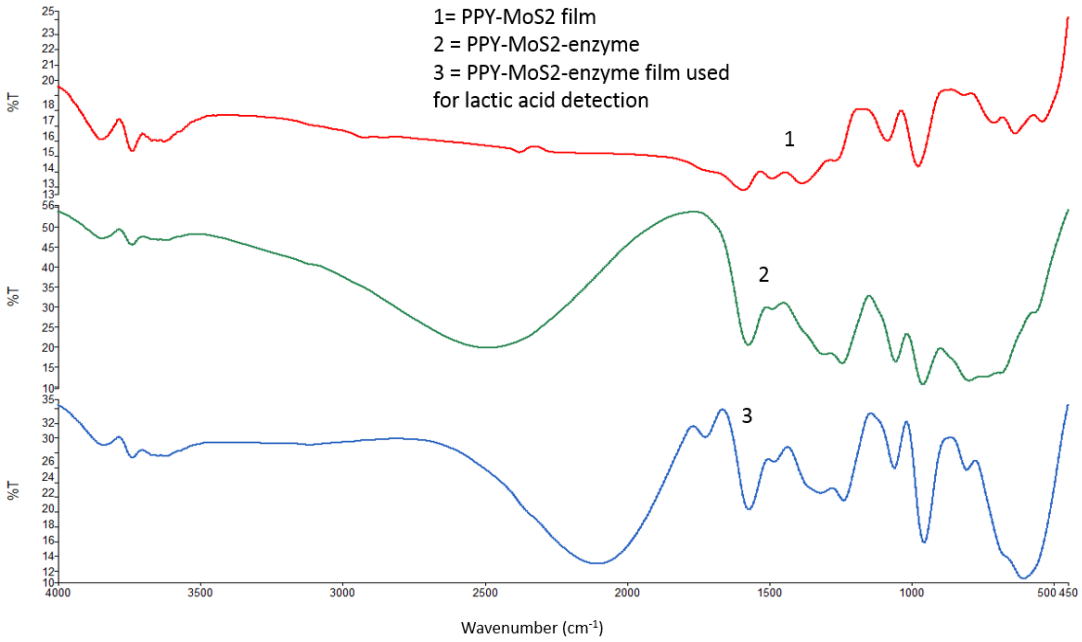

Figure 22. FTIR spectra of PPY-MoS_2 (1), PPY-MoS_2-lactate oxidase (2) and PPY-MoS_2-lactate oxidase film used for sensor (3).

Table 4. Characteristic peaks of PPY-MoS_2, PPY-MoS_2-enzyme, PPY-MoS_2-enzyme lactate oxidase film used for sensor.

cm^{-1}	PPY-MoS_2	PPY-MoS_2-enzyme	PPY-MoS_2-enzyme lactate oxidase film used for sensor
C-H stretching	3834	3842	3840
O-H stretching	3738	3739	3737
N-H stretching	3628	3627	3628
PY ring	2378	2491	2105
C=C bending	1590	1574	1725
C-C and C-N bending	1490		1572
Mixed bending with C-N and $-CH_3$ symmetric	1384	1244	1319
C-O and C-H vibration	1085	1056	1238

Table 4. (Continued)

-OH, S-O	977	960	1060
C-H	712	798	955
S-S	636		805
N-H wagging	540		606

4.4.2 SEM

In addition to the chemical properties of molybdenum disulfide, it is of interest to analyze the structural properties of molybdenum disulfide. This is achievable through the use of field emission SEM tools.

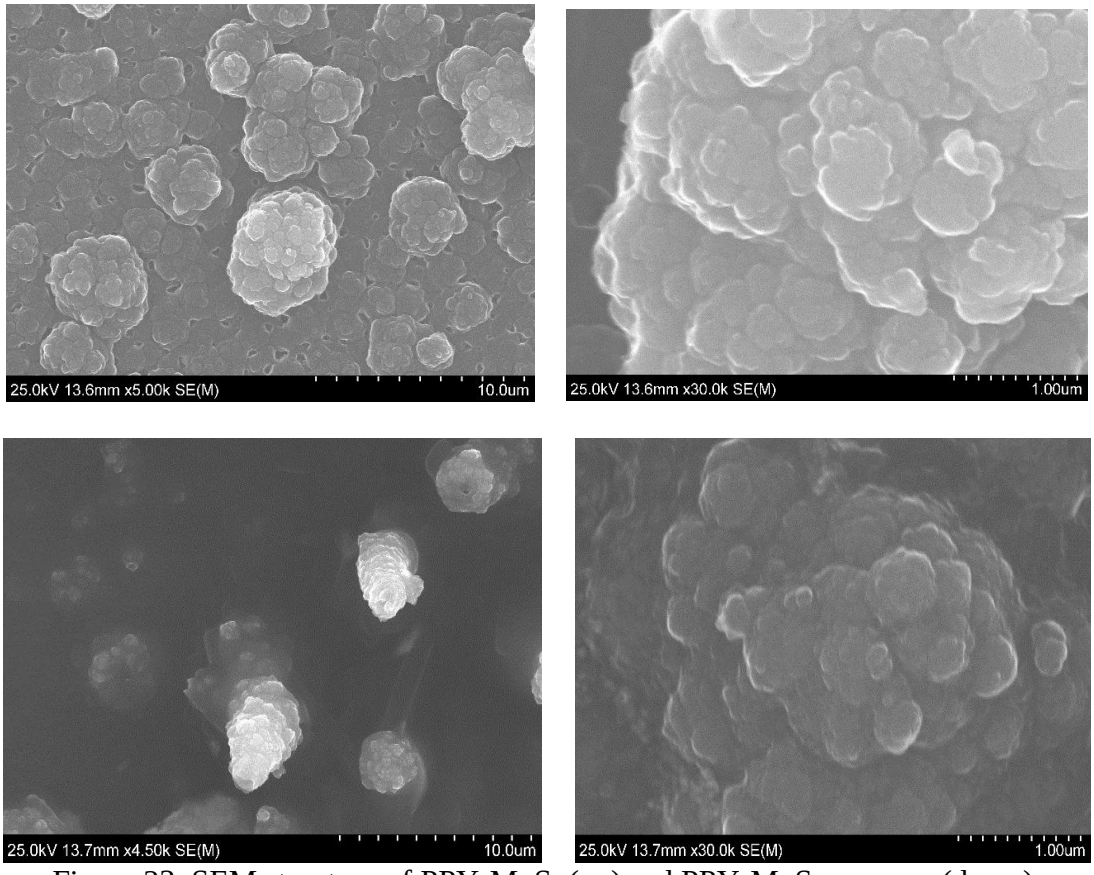

Figure 23. SEM structure of PPY-MoS_2 (up) and PPY-MoS_2-enzyme (down).

Figure (23) shows the physical structure of PPY-MoS_2 film with and without enzyme under the emission of 25KV. Apparently, except the light cause some differences on the brightness, there is no structure change between the two types of films. That illustrate the lactic oxidase will not change the structure of PPY-MoS_2 film.

4.4.3 XRD

XRD measurement of the PPY-MoS_2 film in figure shows two highest peaks appear at 14.4 °, 37.7 ° which perfect match with the MoS_2 peaks. All the diffraction peaks can be indexed to the MoS_2. And there is a low energy peak occurs in figure (24) at peak 26.5 ° could belongs to PPY. According to the literature, the peak of the PPY should occurs at 25 °. The peak position has shifted, compared with the reported of PPY materials, which may result from the amorphous structure of PPY or due to PPY doping into MoS_2. However, no other form of crystallinity are shown consistent with XRD result in figure (18). The figure (25) present same peaks as figure (24) and additional peaks at 2Θ=31.7°, 2Θ=33.7°, 2Θ=51.5°, 2Θ=54.8°, 2Θ=61.6°, 2Θ=65.6°, and 78.7°. These peaks are attribute to the lactate oxidase. Also we can recognize that the peak of PPY at 2Θ=26.5° becomes obvious. That indicates lactate oxidase has not changed the crystallinity of PPY-MoS_2 film moreover lactate oxidase's gentle characterization will promote polymer's functional.

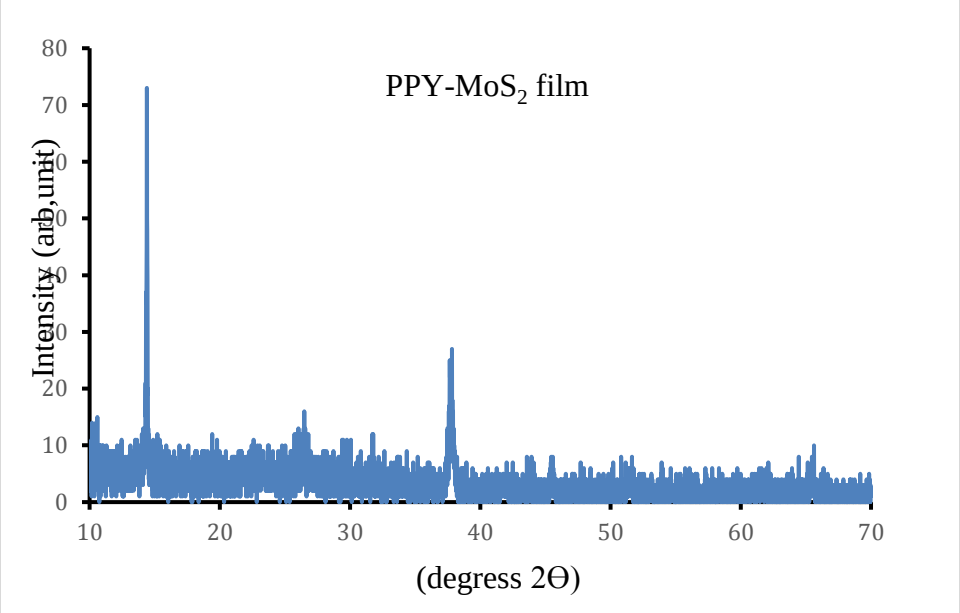

Figure 24.XRD measurement of the PPY-MoS_2 film without lactic oxidase.

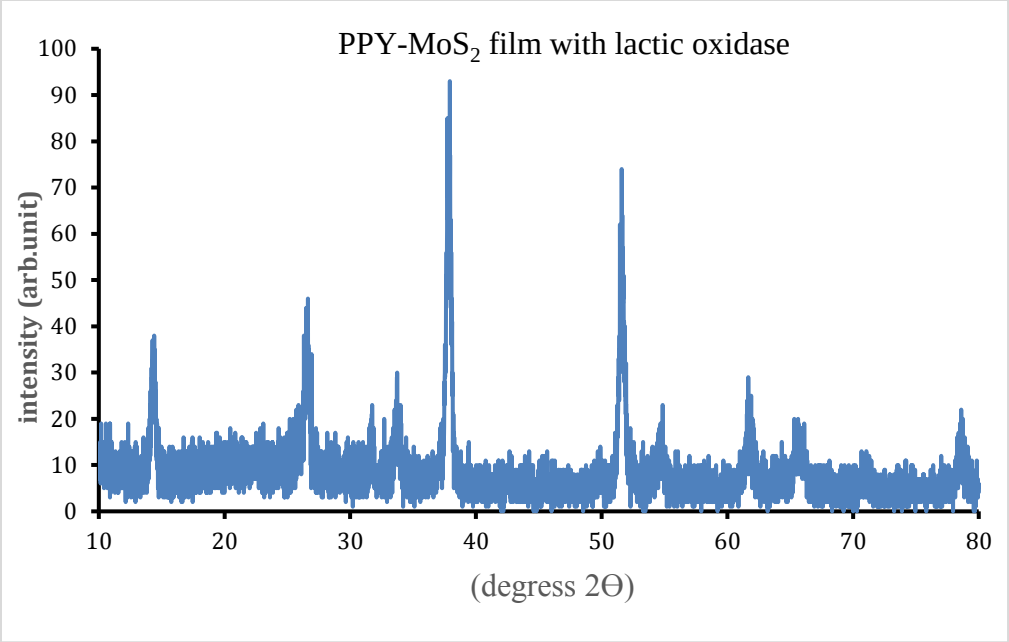

Figure 25.XRD measurement of the PPY-MoS_2 film with lactic oxidase.

4.4.4 UV-Spectroscopy

Figure (26) shows the wavelength between PPY-MoS_2 film with and without lactic oxidase. The curves are almost the same but a shift occurs on the PPY-MoS_2 film with enzyme. This is caused by an altered molecular arrangement of the PPY-MoS_2 film with enzyme. The experiment result depicts that the enzyme will rearrange molecular's positon and provides the PPY-MoS_2 film a better conductivity compared to PPY-MoS_2 film without enzyme.

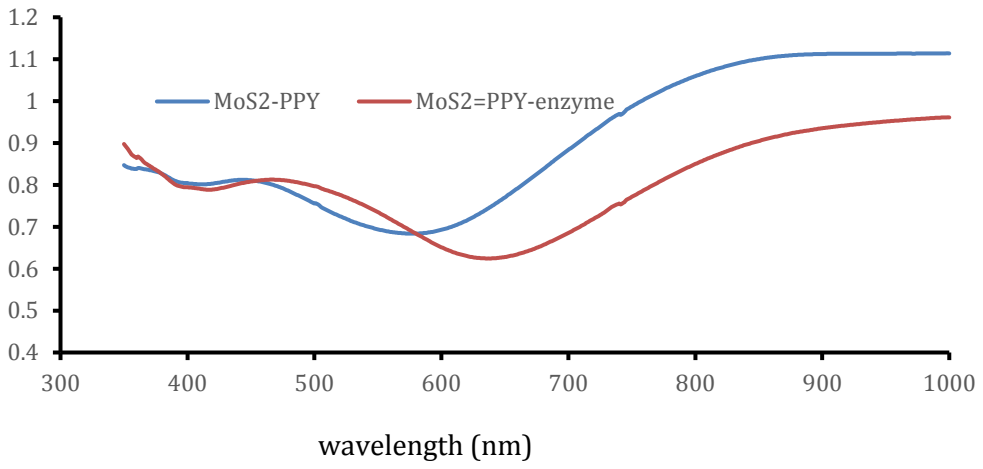

Figure 26. UV spectra of PPY-MoS_2 film without and with lactic oxidase.

4.4.5 Raman

Figure (27) shows the Raman spectra of PPY-MoS_2 film without (red) and with lactic (blue) oxidase immobilized within it. The absorption Raman shift is similar to one observed in FTIR studies. There is Raman shifts are observed at 891, 1056, 1217, 1602, 1961, 2268, 2373 and 2744 cm-1 for PPY-MoS_2 film. The Raman shift are observed at 994, 1061, 1352, 1432, 1594 and 2584 cm-1. The presence of oxidase is dominant as previously observed from FTIR and X-ray diffraction studies.

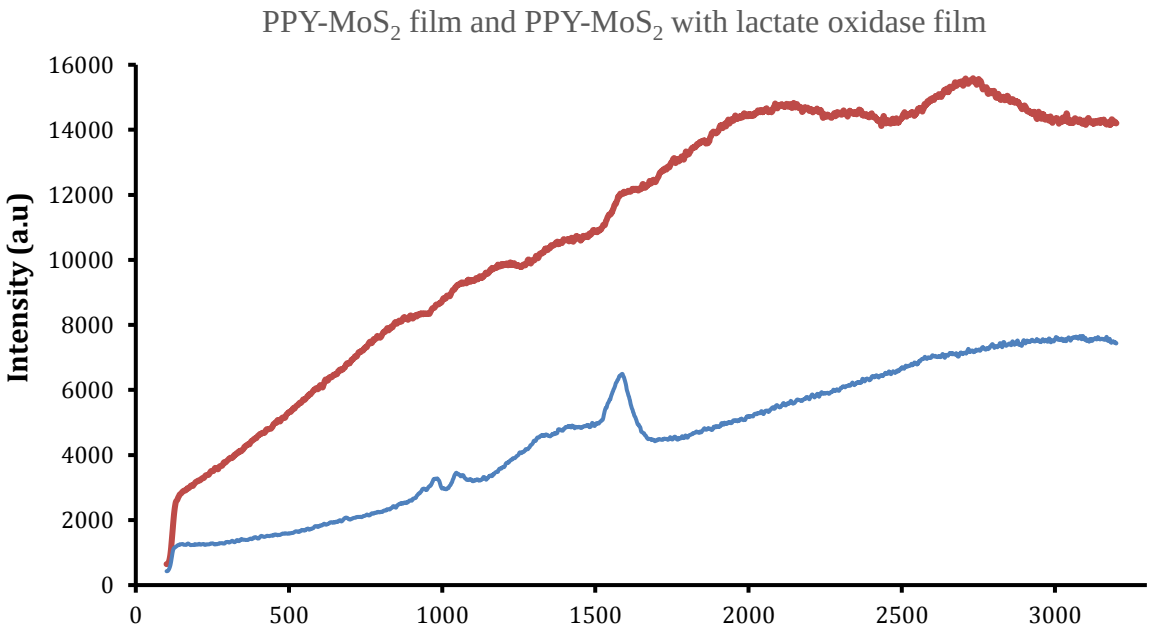

Figure 27. Raman spectra of PPY-MoS_2 film without (red) and with lactic (blue) oxidase.

4.5 Types of Dopant Used

There are a number of types of dopants that can effectively be used in MoS_2-PPY films used for biosensor applications including as lactate sensors. Some of the common dopants normally used include chlorine, sulfonate and paratotule. For example, chlorine is an important type of dopant that is widely used in diverse semiconductor applications. It is known that chlorine is an important anionic dopant material that can significantly enhance the physical and electrochemical

properties of thin MoS_2-PPY films. This is particularly attributed to the significant effects of chlorine on electrical, morphological and optical properties of semiconductor films such as MoS_2-PPY films [84].

The addition of chlorine into the film it is likely to reduce the particle sizes with increasing concentration of chlorine. Similarly, the addition of chlorine also results in a shift in the optical band gap. Generally, the chlorine atoms induces magnetic moment which initiates from the dopant for molebdenum (Mo) d orbitals. MoS_2 nanomaterial has magnetic features whereas chlorine doped systems reveals half-metallic ferromagnetism [85]. However, chlorine atoms integration into a MoS_2 monolayer is difficult than fluorine doped systems [76].

On the other hand, sulfonate is another important dopant material that can effectively be used to dope PPY films. This is primarily attributed to the presence of p-doping of organic anions in sulfonate such as sodium sulfonate. This enables the composite material (MoS_2-PPY films) to selectively sense in a wide range of electrochemical environments.

Finally, paratolune doping materials has also be used in the modification of the conductivity of semi-conductors [86]. The effects of synergy are attributed to dual decoration locations formation of the MoS_2 slabs, with the maximum activity attained at a loading between 0.25 and 0.5 wt percent Ru has some doping effect [74]. MoS_2 cake like structure can be obtained by decomposition of naphthenate [87]. The carbonaceous species that are scattered over the sulfide particles avert MoS_2 slabs from sintering, have an effect on the reactants accessibility to MoS_2 surface and as a result, affects the catalytic activity of the sulfides. The doping nearly has no influence on the dispersion, coordination state and textural characteristics of the catalysts MoS_2 [76].

There is no element of halogen family that is an effective dopant when serves as an adatom dopant. Nevertheless, when high density sulfur atoms are substituted by the atoms of chlorine, the discrete impurity energy levels in molybdenum sulfide widen into a band and combine with conduction band. It results in the narrowing of the band gap and degeneration doping. In contrast, a considerable quantity of chlorine is detected on the surface of the flakes the utilization of Secondary Ion Mass Spectrometry although the technique for molecular doping materials is systematically rinsed b isopropanol and acetone [88]. The chlorine normally attacks the MoS_2 at high temperatures to form the molybdenum pentachloride. Since the sulfur vacancies are broadly detected from the mineral molybdenum disulfide, there is an assumption that the effect of doping is attained through additional electrons donated by chlorine atoms when they take up the location of the sulfur vacancies. The contact resistance MoS_2 reduces significantly following doping.

The stable biochemical interface is required for biorecognition. It assists in creating stable, effective and reproducible biotransducers [75]. The seeding layer enhances the loaded enzyme activity. It offers a surface that enables enzyme adsorption without changing the natural qualities. The PPY has a stabilizing influence on the enzymes. The seeding layer considerably reduces the average biofabrication time for the unseeded biotransducer and seeded biotransducer. It helps in improving the reproducibility in biofabrication.

4.6 Characterization of Doped Film

Doped films share a diverse number of characteristics. This is particularly attributed to their similar optical, physical and electrochemical parameters some of which may include improved band gap energy, extinction coefficients as well as refractive index among others. These characteristics are critically important when it comes to understanding the behavior and efficiency of the doped films [84]. However, the characteristics of the doped films may also be affected by

other factors such as the concentration of the doping material or element as well as the conductivity and thickness of the p-layer.

Dopant material elements can be added to significantly enhance the physical and electrochemical properties of thin semiconductor films. For example, the addition of a dopant can potentially shift the Fermi levels contained within the material thereby resulting in a material with more positive (p-type) or negative (n-type) charge carriers relying on the variety of the dopant. According to[85], a dopant is an important trace impurity element that is normally added in low concentrations to help alter the optical or electrical properties of the substance. This is particularly attributed to the significant effects of chlorine on electrical, morphological and optical properties of semiconductor films such as MoS_2-PPY films.

Generally, the band gap of MoS_2 and its Fermi energy can be measured using both the scanning tunneling microscopy and scanning tunneling spectroscopy with the getting abilities. They can also be used to track its behavior and evolution of its gate voltage. Finally, by using spectroscopy, the source of n-doping in MoS_2 can be traced in order to determine defects if any, which attribute to S vacancies. In the case of layered MoS_2-PPY, there is a high level of n-doping, which cannot be attributed to the S vacancies. Consequently, it can be deduced that n-doping of a thin-filmed layer sample occurs because of the charge traps at the interface of the substrate.

4.6.1 Cyclic Voltammetry

4.6.1.1 Comparison with and without Lactic Acid

Figure (28) depicts the change in curves between the PPY-MoS_2-enzyme electrode in phosphate buffer with and without 0.01 m lactic acid. The current increases from 15 to 20μA as compared with that in the buffer than 0.01 mM lactic acid solution. This is due to the catalytic

reaction of the PPY-MoS_2-enzyme electrode with L-lactic acid. The peak appears at 20 μA which is attributed to H_2O_2 generation during the lactic acid oxidation due to lactate oxidase.

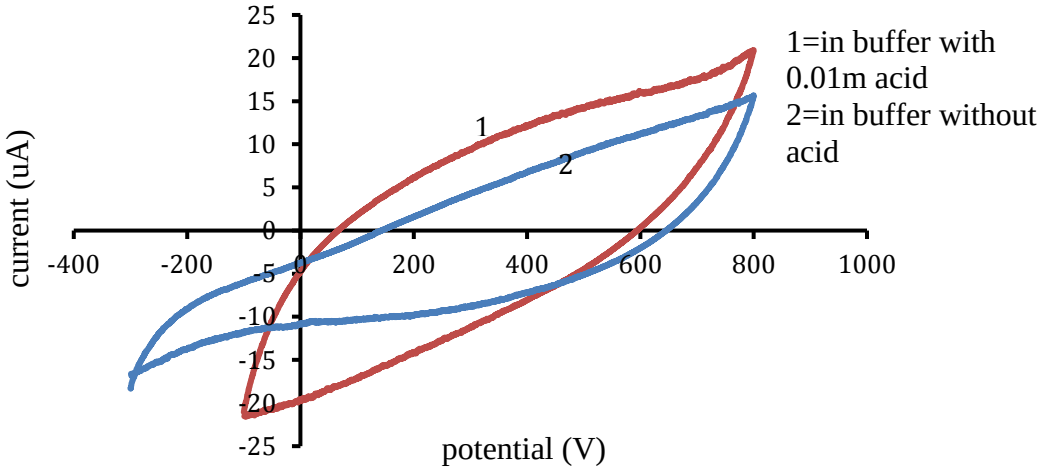

Figure 28. CV of PPY-MoS_2-enzyme in buffer with and without lactic acid.

4.6.1.2 Comparison to Different Scan Rate without Lactic Acid

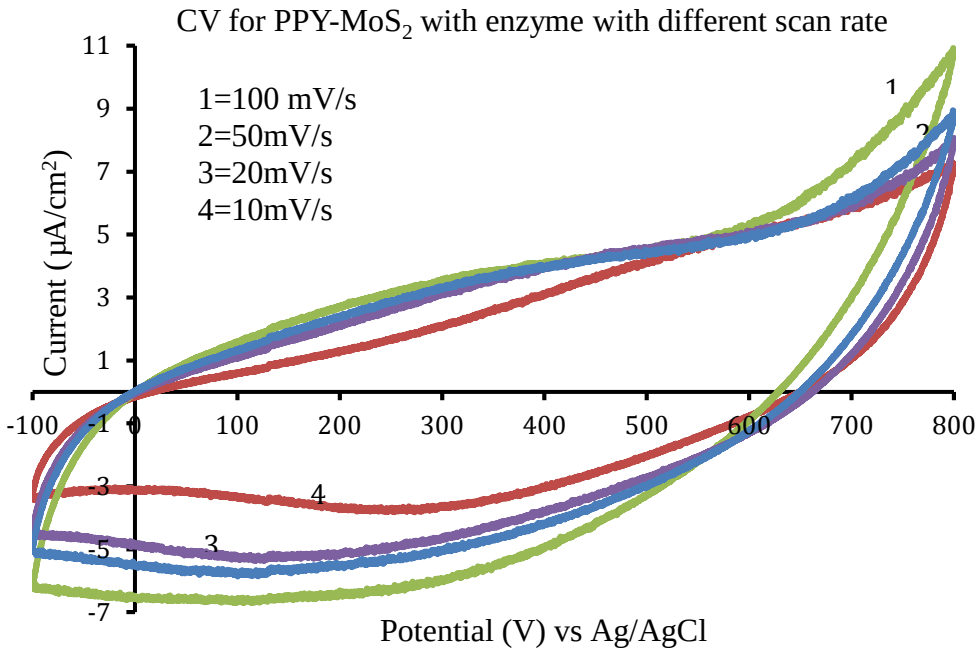

Figure 29. CV of PPY-MoS_2-enzyme in buffer without lactic acid in different scan rate.

Figure (29) illustrates the CV curves of the PPY-MoS_2-enzyme electrode in the buffer without lactic acid at various scan rates of 10, 20, 50 and 100 mV s^{-1}, respectively. The CV curves shows

the peak current rise at the increase of scan rate. The experiment result proves that the oxidation and reduction reactions are changed by the enzyme and lactic acid in the solution.

4.6.1.3 Comparison to Different Scan Rate with Lactic Acid

Figure (30) illustrates the CV curves of the PPY-MoS_2-enzyme electrode in the buffer at various scan rates of 5, 10, 20, 50 and 100 mV s^{-1}, respectively. The redox current rise in CV with increase in scan rate is related to diffusion-controlled electrochemical behavior.

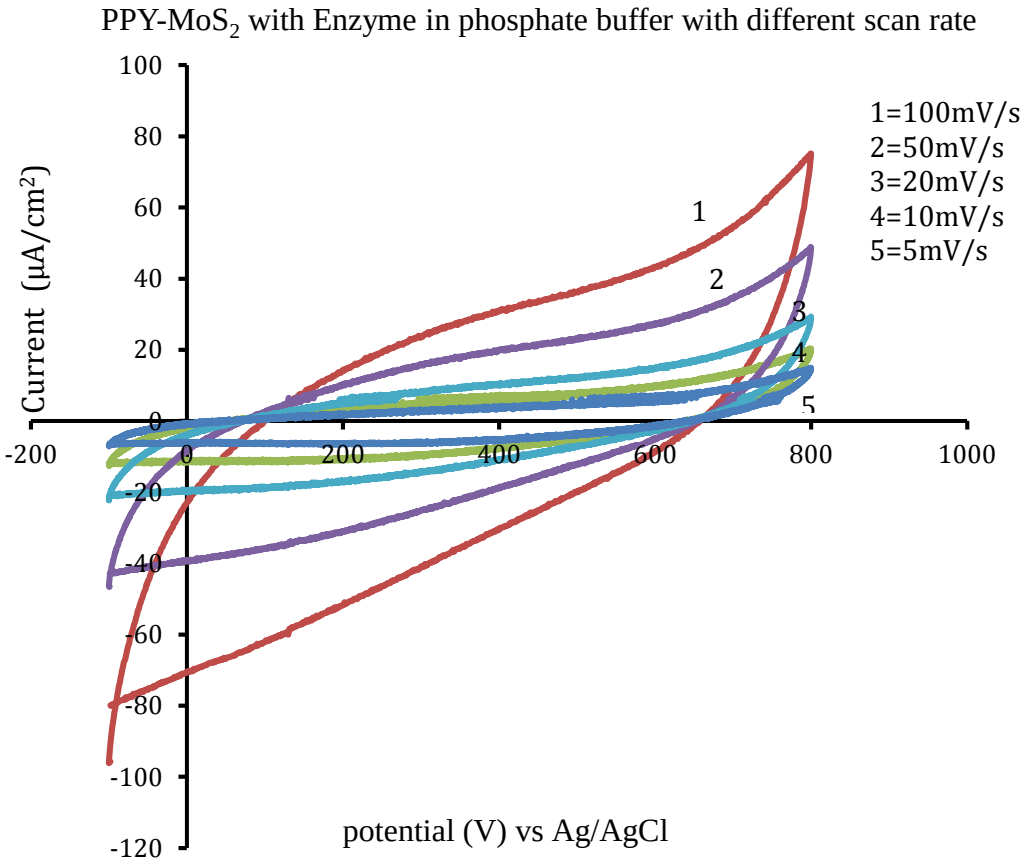

Figure 30. CV of PPY-MoS_2-enzyme in buffer with lactic acid in different scan rate.

4.6.2 Chronoamperometry

In this experiment, lactic acid was added 100/s at once while being stirred to have a stable current value as it is shown in Figure (31). Because the atmosphere pressure is a constant and the concentration of the O_2 in the phosphate buffer is constant so all the catalytic signal changed can

be observed should be attributed by the change of lactic acid concentration. As the Figure (30) reveals that amperometric current rises due to addition of lactic acid concentration. It takes appropriate 20-30 seconds to make the current to become a steady state again.

Figure (32) shows calibration curve of the lactic acid biosensor. However, lactic acid concentration increase displays linearity for the current density rise from 2 to 9 μA cm^2.

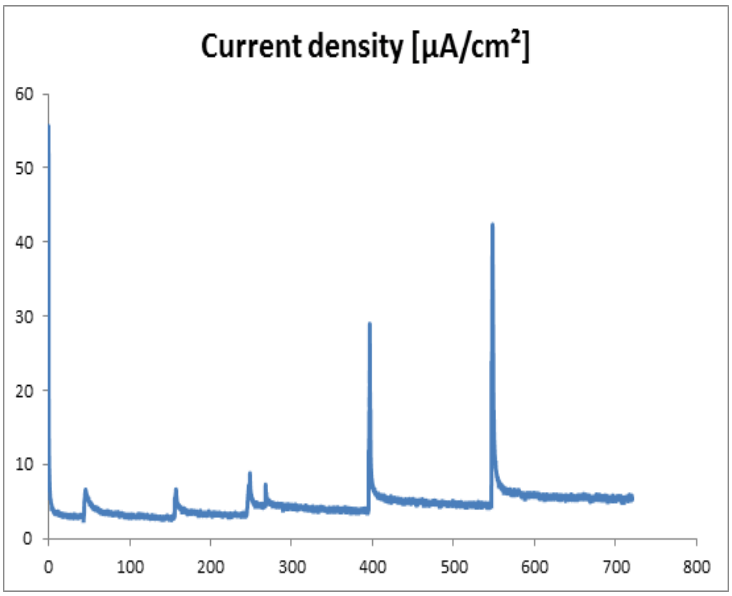

Figure 31. PPY-MoS_2 film with oxidase current test in lactic acid concentration from 0-0.2mM.

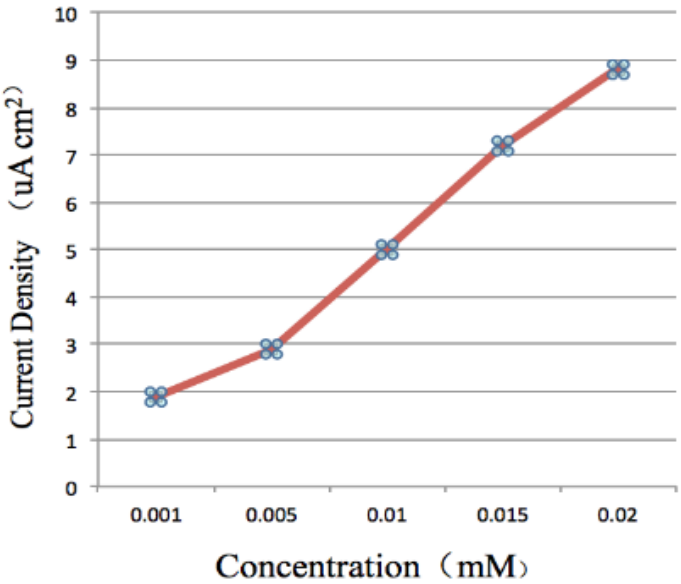

Figure 32. Lactic acid response curve.

4.7 Lactic Biosensor Application

Lactate is an important metabolite that is normally formed as result of the anaerobic metabolism of glucose in the body muscles. A number of researches within the last few years have increasingly focused on developing ways of sensing the production of lactate due to its critical importance in clinical care, food processing and sport medicine. One of the commonly used electrochemical lactate biosensors is Amperometric enzyme biosensors which particularly work by measuring the magnitude of current between reference and working electrodes. In the medical field, biosensors are increasingly being applied in a wide range of areas such as the detection and determination of the concentration of the neurotransmitters. For example, when the MoS_2 is used as an electrode in the lab testing process, it is possible to confirm the levels of glucose and neurotransmitters in the body. According to many experts, this can be medically used in the medical handling of Parkinson's disease, schizophrenia, and Tourette's syndrome among others.

Molybdenum disulfide, MoS_2, was previously used in as a lubricant and a catalyst in the petroleum refinery process. However, the scientific discovery that MoS_2 can be used as a single layer biosensor has brought tremendous advantage in the research field. The field of application of this biosensor includes the biological detection of the presence of analytes in given solutions. This capability of the biosensor to detect the small molecules and analytes can be applied in medical research. The study of DNA makeup and structure can be achieved through the use of MoS_2 as a bio-sensing medium. The world of forensic investigation benefits greatly with the use of MoS_2 in the examination of protein molecules and DNA in the samples of interest. Moreover, the agricultural sector can employ the biosensor in analyzing the plant cells in agricultural research initiatives [91].

The high sensitivity that is inherent in MoS_2 as a biosensor is of immense advantage to the researchers. This biosensor is manufactured using the field effect transistor techniques that make it highly sensitive as a biosensor. According to Pumera and Loo [92], the MoS_2 is non-destructive to the samples being observed. The efficiency of the research is enhanced since the samples' characteristics are not destroyed. In cases where the samples were disfigured, the quality of the results that were derived from them was compromised. The fact that MoS_2 does not destroy the sample implies high-quality results. The other key trait of MoS_2 biosensor is real-time detection. The real-time detection ability improves on the timeliness in research work. The reduced experiment times implies reduced costs and predictable timelines for experiments and research work.

Moreover, the biosensor can be scaled to down to fit the size of the sample being studied. The ability to produce the MoS_2 in large-scale provides a cost-benefit to the researchers. The large sheets can be divided into smaller sheets to suit the specimen being studied [93].

In nanotechnology, MoS_2 has been used in electrochemical investigations in the molecules in the cells. The medical field has employed this high-sensitive biosensor in the detection and determination of the concentration of the neurotransmitters. When the MoS_2 is used as an electrode in the lab testing process, it is possible to confirm the levels of glucose and neurotransmitters in the body. This can be medically used in the medical handling of Parkinson's disease, schizophrenia, and Tourette's syndrome [94].

The use of the molybdenum biosensor has been adopted in the security sector in bio-identification initiatives. The security agents use the biosensor to reconcile the biological elements from the specimen against the suspects. This can be used in the forensic investigation in the security sector. The elements that are investigated are enzymes and the antibodies. MoS_2 allows

for the testing of the presence of chemical elements in samples. This can be used in the investigation of weapons used in a crime. Finally, MoS_2 can be used in the environmental research. It helps in the monitoring and measurement of the composition of atmospheric elements by the examination of a part of an organism. The chemical elements can be tested to determine their presence and concentration. This helps the environmentalists to make appropriate policy decisions based on the evidence provided through the bio-research.

4.8 Stability

The concept of stability in this context can be viewed in terms of thermal stability of polymers such as PPY. Many organic polymeric materials such as PPY melt at temperatures below 150^0C. At the same time, many of them degrade at a rapid rate in temperatures above 200^0C. Polymers that are thermally stable are considered to withstand high temperatures without losing their strengths or changing their chemical structures. Polymers with the ability to withstand up to 500^0C are said to be stable and are highly aromatic in structure. They have high melting points, some of them are infusible, and they have low solubility in all solvents.

Thermal stability is important stability in polymers used for electrochemical purposes, although none can withstand up to a temperature of 500^0C for a substantial length of time [72]. Because of the application of PPY as a conducting polymer in elevated temperatures, determining its thermal stability has both fundamental and technological significance. It is also essential to determine its environmental stability at elevated temperatures to show its suitability in use for making lactate sensor with the MoS_2.

CHAPTER 5. CONCLUSION AND RECOMMENDATIONS

In summary, electrochemical biosensors work has been analyzed using biological activity through identification of the electric signals of biological activities by transducers. The two dimensional molybdenum disulfide MoS_2-PPY films belong to one of the most stable classes of inorganic graphene analogs that possess an intrinsic finite bandgap that are particularly suitable in use in a diverse range of biosensor applications. Generally, MoS_2 has recently drawn considerable interest regarding their potential use as biosensors due to their unique physicochemical properties associated with their quantum size and their ultra-thin structure. The MoS_2 has a great potential as a transducer material in future biosensor applications.

Additionally, MoS_2 is widely used in biosensing area due to its comparatively simple synthesis procedure and simple growth on substrates. The field effect transistor centered biosensing device with the MoS_2 acting as a channel leads sensitive biosensor. The FET technique is used to manufacture the sensitive biosensor. The MoS_2 has good detection limits, high fluorescence quenching capability a quick response time in the optical kind of biosensors.

The nanocomposites that contain MoS_2 alongside the graphene and the metal nanoparticles are efficient transducers for biosensor applications. The MoS_2 can be utilized as a single layer biosensor. The biosensor can be applied in the biological detection of the existence of analytes in specified solution. The biosensor's detects the analytes and trivial molecules in the field of medical research. The utilization of MoS_2 as a biosensing medium can assists in the studies concerning the DNA structure and components.

Over the last few decades, nanostructured electrode materials like MoS_2 have been applied in various biosensor applications. For example, MoS_2 is currently one of the most promising materials for a wide range of electrochemical applications used in many fields including pharmacology, pathogen detection, environmental monitoring and glucose monitoring. In the medical field, biosensors are increasingly being applied in areas of detection and determination of the concentration of the neurotransmitters, glucose sensing, cholesterol sensing and several anions and cations in the human samples. Additionally, several recent researches within the last few years have increasingly focused on developing ways of sensing the production of lactate due to its critical importance in the determination of biological analytes such as cholesterol, glucose and dopamine among others.

Generally, the MoS_2 nanosheets are prepared by hydrothermal processes at temperatures of 200 ℃. MoS_2-PPY film possesses a diverse range of electrical and chemical properties that particularly make them suitable for their bio-sensing applications in various fields. The key benefits of using MoS_2-PPY film in biosensing include high sensitivity, improved conductivity. The doped films of PPY become brittle materials, and they attain stability at from the atmospheric temperature to about 1500C upon which the dopant begins to evolve. The PPY oxidation enhances its ability to be an electric conductor.

CV is conducted by cycling the working electrode potential and then measuring the resultant current. It is used during the doping of the MoS_2 and PPY. It helps in determining the concentration of unknown solutions by creating current vs. concentration curves. The CV is utilized in the qualitative study of information concerning electrochemical processes under distinct conditions. These include the existence intermediary chemicals and compounds throughout the oxidation and reduction reactions in addition to the reversibility processes.

Resistance is the ability of elements in an electric circuit to resist the electric current flow. The impedance measures of the ability of the circuit to resist for the electrical current flow. The impedance of the ion solution relies on the concentration of the ions in the solution and other aspects such as the temperature and the type of ions. Chronoamperometry is a pulsed technique that generates high amounts of charging currents and this current takes a transient form and decays exponentially with respect to time like any RC circuit. In many electrochemical cells such as those in MoS_2-PPY, this current decay is much slower compared to the charging decays.

The potential application of molybdenum sulfide in electrochemistry, catalysis, lubrication and a host material for intercalation chemistry has led to a growing interest in the synthesis of the sulfide. The MoS_2 that is utilized in lubricant applications is in purified form of the mineral molybdenite. The MoS_2 lubricant grade that is in a commercial form has a hexagonal layer lattice crystal structure that gives it an exceptional adherence to numerous metals and low friction. MoS_2 can be used in the environmental research. It helps in the monitoring and measurement of the composition of atmospheric elements by the examination of a part of an organism. The X-ray diffraction is used to establish the crystallinity of molybdenum disulfide. The X-ray diffraction tests that have been done on MoS_2 have confirmed the crystallinity of the nanosheets. The sheets are observed to be polycrystalline with hexagonal structures.

In the manufacture of semiconductors like MoS_2-PPY films, a dopant is an important trace impurity element that is normally added in low concentrations to help alter the optical or electrical properties of the substance. This is particularly because of the crystalline nature of the atoms of a dopant. This may result in change in electrical properties of a semiconductor. Doping elements can lead to a realization a high level synthetic control and reproducibly MoS_2 for certain synthesis of MoS_2. Doping normally results in a diverse number of effects on semiconductors like MoS_2-

PPY films. Doped films share a diverse number of characteristics. This is particularly attributed to their similar optical, physical and electrochemical parameters some of which may include improved band gap energy, extinction coefficients as well as refractive index among others.

The doping helps in creating a bandgap and determining the Fermi energy in the molybdenum disulfide. The doping of the molybdenum sulfide monolayers with the rhenium and introducing the gold adatoms augment the local chemical affinity. Chlorine is an important anionic dopant material that can significantly enhance the physical and electrochemical properties of thin MoS_2-PPY films. Sulfonate can be used to dope PPY films. This is primarily attributed to the presence of p-doping of organic anions in sulfonate such as sodium sulfonate. It enables the MoS_2-PPY films to selectively sense in a wide range of electrochemical environments. Besides, paratotulene doping materials can be utilized in the modification of the conductivity of semi-conductors.

CHAPTER 6. FUTURE WORK RECOMMENDATIONS

Future studies regarding the potential application of MoS_2 as a composite material in the construction of electrochemical biosensors should on the stability, sensitivity, cost effectiveness and the detection limits of MoS_2-PPY film biosensors. It is also recommended that future researches should address other related copolymers that can effectively be used to enhance the performance of biosensors.

Additionally, future researches should also be centered on the research for the improvement impact of chlorine on the physical and electrochemical properties of thin MoS_2-PPY films. The field effect transistor technique can be utilized to measure the electrochemical properties of chlorine and sulfonate decorated MoS_2 in the further studies. The use of MoS_2 as a nanomaterial for sensing and biosensing applications exemplifies an imminent research study area that needs to be examined. Thus, the findings of this work are expected to have considerable contributions towards the forthcoming DNA biosensors' fabrication. There is the need to have multiplexed varieties of MoS_2 based biosensors for the numerous applications. A drug testing platform should be put in place to permit fast display of the information regarding the interactions amongst the any innovative drugs and their envisioned types of protein target.

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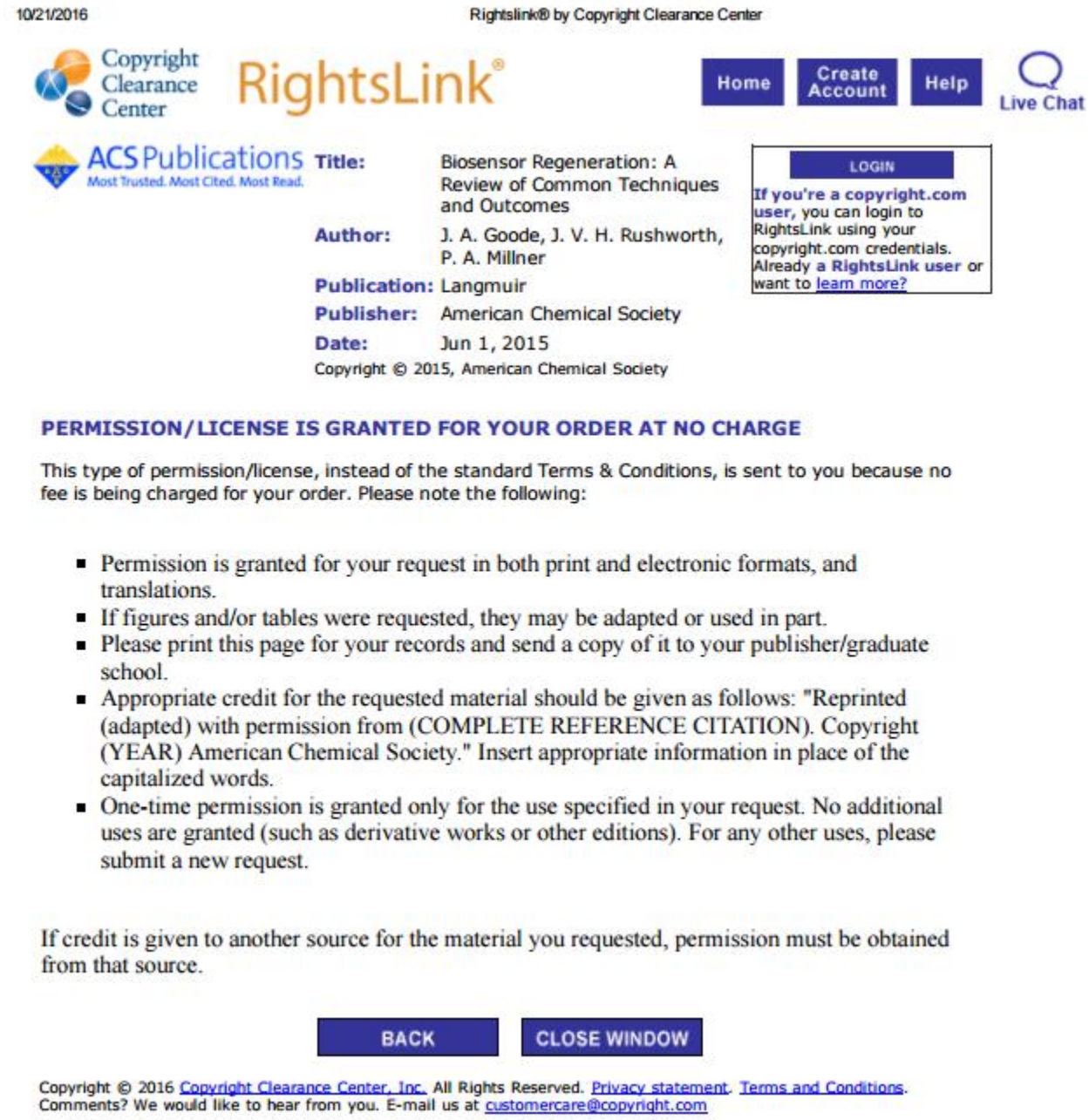

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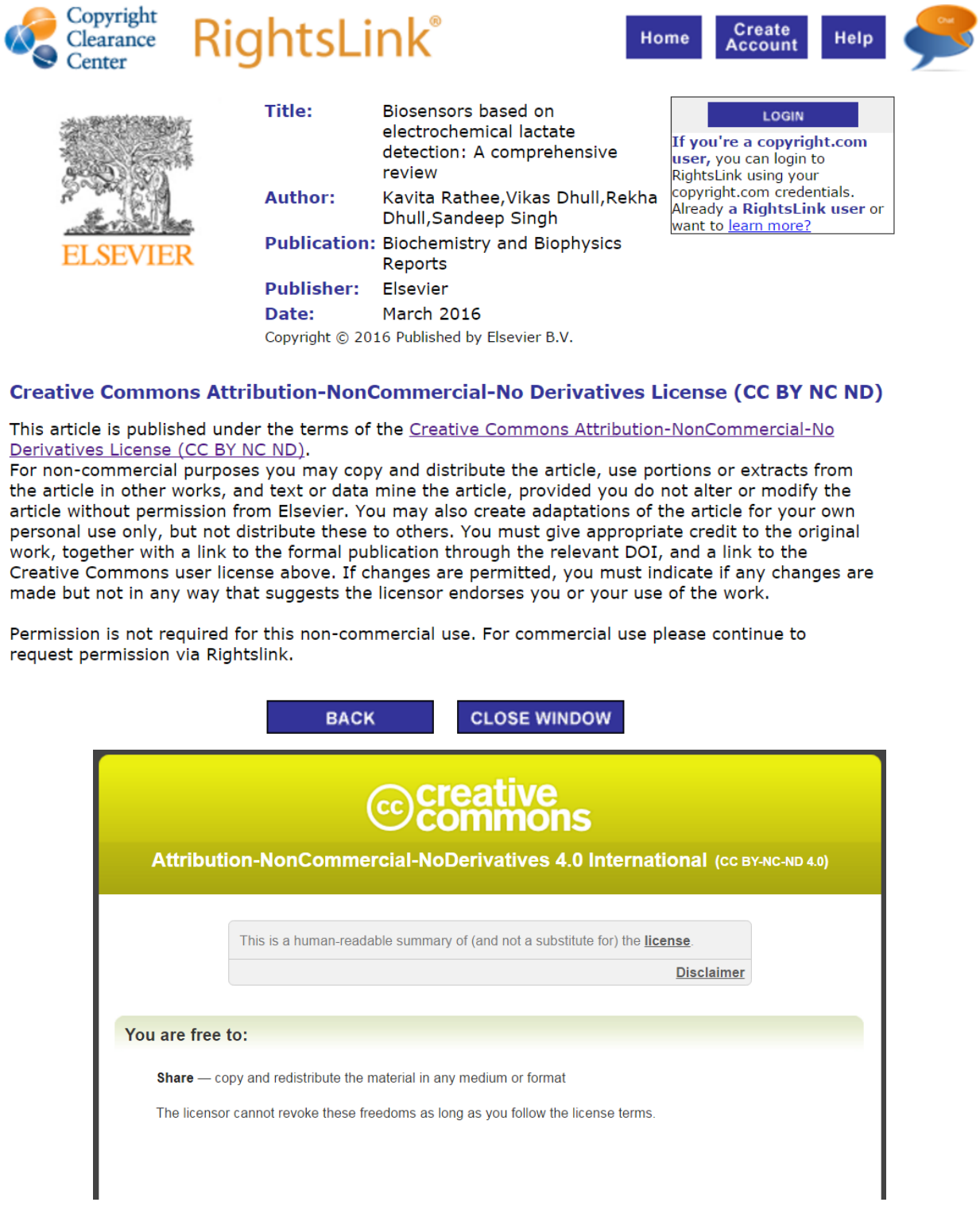

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