Conjugated Polymer of Biosensor using Langmuir-Blodgett Technique– A Review

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Abstract. Health biosensor applications based on conjugated polymer have gained many attentions among researchers because of their sensitivity, selectivity, and linearity. Polyaniline, a conjugated conducting polymer has been explored since the early 1960s and one of the famous conducting polymer compare to the others like polypyrrole, polyacetylene, and polythiophene. Polyaniline is ease to synthesis, high conductivity, and good performance in biosensor applications. A doping approach using protonic acids (hydrochloric acid, 4-dodecylbenzenesulfonic acid, sulfuric acid, phosphoric acid) can be utilized to increase solubility and induce fusibility of the stiff chain of the polymer. A structural modification of doping process could make the polymer become high conductivity and it was universally agreed about that. Polyaniline presents ionic conductivity and electronic combinations that make bio-interfaces exist among the other electrochemical applications. The conductivity of the polymer is one of the promising materials that may be used to improve the analytical properties of sensors. Langmuir-Blodgett technique is a method to produce thin film of polyaniline therefore the conductivity of polyaniline can be measured using four-point probe device.

1 Conjugated polymer

Polymers abound in nature. The polymer can be classified as any natural material or substances that composed macromolecules (large molecules). The polymer also multiples smaller and simpler chemical units of the monomer containing a long chain of molecular structures. Protein and cellulose are examples of polymers in living creatures. Many types of polymers are made up of hydrocarbons, which are carbon hydrogen molecules [1]. These polymers are made up of long chains of carbon atoms connected one to the next, referred to as the polymer's backbone. Because of the nature of carbon, each carbon atom in the backbone can have one or more additional atoms bonded to it. Most of the polymer are insulators, and many researches are still studying to make the polymer could conduct electricity.

Conjugated polymers are organic macromolecules containing a backbone chain of alternating double and single bonds. Their overlapping p-orbitals form a system of delocalized π-electrons with fascinating and valuable optical and electrical features. On the other side, the conjugated polymers are not conductive because they are covalently connected and lack a valence band like pure metal. The doping technique is widely acknowledged as an effective way for producing conducting polymers [2]. Some scientists found that three decades ago after undergoing a structural alteration procedure known as doping, a form of conjugated polymer known as polyacetylene could become extremely electrically conductive. Because it precipitates out of solution as a black, air-sensitive,

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infusible, and intractable powder, it cannot be processed in its linear form [3]. Conducting polymer is an exciting electronic material because of its capability to produce some applications such as bioelectronics, sensors, biomedicals and many more. Conducting polymers have a special property like mixed ionic electronic conductivity, biocompatibility, and mechanical softness that make them famous in biology and electronics [4]. Other properties include charge carriers, concentrations of carriers and effect of impurity [1].

2 Properties of polyaniline

Researchers are interested in studying the conductivity, production, and characterization of polyaniline, which is one of the most attractive conductive polymers. The applications of polyaniline are widely used in nanoelectronics, nanosensors and nanomaterials [5]. Polyaniline presents ionic conductivity and electronic combinations that make bio-interfaces exist among the other electrochemical applications [6]. Polyaniline-based compositions' electrical conductivity may be precisely regulated across a large range. Polyaniline is a \( p \)-type semiconductor with a large number of holes as charge carriers. The semi-conducting capabilities are due to the delocalized bonds present in the system. Its electrical conductivity is primarily determined by molecular weight, crystallinity percentage and inter-chain separation, oxidation degree and molecular arrangement, and doping percentage and others [7].

Low cost, more stable, easy to synthesis, and a special doping/dedoping mechanism make the polyaniline a unique position among the other conductive polymers [8]. Polyaniline, on the other hand, has a limited number of cases of poor solubility in most organic solvents and weak chemical reactivity of protonic doping [9]. Protonic doping means it can only react in a relatively strong acidic condition which is less than four of pH reading. Examples of protonic acid are hydrochloric acid (HCl), sulfuric acid (\( \text{H}_2\text{SO}_4 \)), hydrobomic acid (HBr), nitric acid (\( \text{HNO}_3 \)) and acetic acid (\( \text{CH}_3\text{COOH} \)). Sulfonic acid (-SO\(_3\)Na or -SO\(_3\)K) [10], boronic acid (-BO\(_2\)H\(_2\)) [11], and carboxylic (-COONa) groups at the phenyl rings or nitrogen sites of polyaniline were found to be the simplest and most cost-effective strategy for addressing these difficulties in a previous study. [12]. However, the chemical and electrical characteristics required for polyaniline design for practical applications are unknown as a result of derivatization at the phenyl ring and nitrogen sites at the atomic level.

According to some reports, polyaniline exists in different coloured powder [13]. The most extensively used synthetic method to polyaniline is aniline oxidation, which can be done electrochemically or chemically. The reaction is commonly done in an acidic medium using chemical oxidizers such as ammonium persulfate. Polyaniline can be found in a number of different oxidation states. Polyaniline can occur in several well-defined oxidation states. The multiple states extend from totally reduced leucoemeraldine to totally oxidized pernigraniline, via protoemeraldine, emeraldine, and nigraniline [14]. Unlike other polyaromatics, polyaniline’s completely oxidized form is not conducting, and neither are the others. Polyaniline becomes conducting when the moderately oxidised states, notably the emeraldine base, are protonated and charge carriers are generated. This mechanism, known as protonic acid doping, is what distinguishes polyaniline. To conduct, no electrons must be added or removed from the insulating material. Leucoemeraldine base (LEB) which is present in violet color, emeraldine (EB) in dark copper color and pernigraniline base (PNB) in colorless [15]. The chemical structure of polyaniline consists of long chain [16] and the doping/undoping process is exaggerate by a oxidation and reduction process of hydrogen atom [17].

The colour change associated with polyaniline in various oxidation states can benefit sensors and electrical devices. While colour is useful, the best method to construct a polyaniline sensor is to use of the vast variances in electrical conductivity between various
oxidation states or doping levels. Polyaniline may be optimized for specific purposes using various synthesis methodologies and modification approaches [18]. Polyaniline has numerous advantages to investigate, particularly in medical applications. Polyaniline wide and controllable range of conductivity. Conductivity values of up to 100 S/cm may be attained with pure polyaniline compositions. In melt processing, polymer blends with polyaniline compositions can obtain conductivity values ranging from less than $10^{-10}$ to $10^{-1}$ S/cm, and in solution processing, 10 s/cm [19]. Besides that, polyaniline is a melt and solution-processable polymer that may be processed using traditional processes including blow and injection molding, film casting, fibre spinning, and extrusion. These compositions can sustain temperatures as high as 230-240 °C for short periods (5-10 minutes) without losing their electrical characteristics and they can be melted with a variety of commercial polymers. Moreover, polyaniline also forms conductive blends with a wide range of commodity polymers (polystyrene, polypropylene, polyethylene, PVC, and phenol-formaldehyde resins). It may be manufactured using the standard solution and melt processing procedures. Last but not least, polyaniline functions as processing aids in addition to providing conductivity and the transparent electrically conductive products can be made using polyaniline-based compositions [20].

3 Langmuir Blodgett technique

There are many techniques to make a single or multi-layer film with correct control of its density, molecular orientation and thickness. Langmuir Blodgett is an example of a technique that used mainly by the scientists to make films. One of the few ways for producing structured molecule assemblies, which are required for molecular electronic devices, is the Langmuir Blodgett (LB) process [21]. The LB technique is a method for fabricating ultrathin nanostructured films with a controlled layer structure and crystal parameter, with applications in optical and molecular electrical devices, as well as signal processing and transformation. [22]. LB moves the sample vertically through the monolayer. The LB method allows for continuous variation in material density, packing, and arrangement by compressing and expanding the film with polytetrafluoroethylene barriers (PTFE). By repeating the deposition procedures, nanoscale films of any thickness may be created.

Hydrophilic and hydrophobic materials can be coated with a monolayer from either the liquid phase or the gas phase employing LB methods. LB is used to creating, modify and study monolayers at either the gas-liquid or liquid-liquid interface. A monolayer film may be considered a two-dimensional solid film with a surface area to volume ratio significantly greater than that of bulk materials once compressed [23]. Materials frequently exhibit surprising new characteristics under these settings. The LB may be used to determine how certain molecules pack together in two dimensions. As a result, it enables the preparation of films with the inter-particle distance control required to exploit two-dimensional (2D) materials in technological applications. Other than that, the deposition scheme during up and downstroke of the LB process involved deposition of first and second layer. The outcome can be seen on the surface-pressure area per molecule (п-A) isotherm graph, which depicts different phases of monolayer at the air-water interface. [21].

A monolayer is structured under compression in a typical isotherm experiment, commencing as a two-dimensional gas phase and progressing through a liquid phase to a completely ordered solid phase. The molecules in the gas phase do not interact with one another. When the surface area is reduced, the molecules become more densely packed and begin to interact. The molecules are perfectly structured in the solid phase, and the surface pressure rises considerably. The collapse point is achieved when the maximum surface pressure is reached, after which the monolayer packing is no longer regulated. LB is less constrained by the molecular structure of the functional molecule than other organic thin
film deposition processes. As a result, it is frequently the only technology available for bottom-up assembly. The creation of these films necessitates a great deal of caution and the use of advanced equipment. This instrument's most important component is a teflon-coated tube filled with distilled and deionized water.

4 Polyaniline biosensor

Infectious illness screening, early diagnosis, chronic illness therapy, health management, and well-being tracking are all applications for biosensors. Improved biosensor technology allows for the detection of disease and monitors of the body's reaction to treatment. Sensor technology is essential for a wide range of low-cost and improved form factor medical devices. Biosensors offer a lot of potential since they are simple, scalable, and efficient to use in industrial processes [18]. Conducting polymers have previously been used in biosensor research because they can be used as immobilisation matrices as well as redox systems [24]. Biosensors are the focus of a rapidly expanding field of study due to their wide range of applications in medicine, pharmacy, environmental monitoring, food and process control, defence and security, and, most importantly, diagnostics.

Polyaniline, a semiflexible conducting polymer discovered in the 19th century, has proven to be a versatile material in all major areas of science and technology, including electrochromic devices such as biosensors. [25]. Adjustable conductivity and electrochemical behaviour by monitoring the surrounding pH, dopant type and doping intensity, polyaniline oxidation state, shape, and other characteristics. Besides that, polyaniline is renowned as a material for biosensor development due to its utility as an enzyme entrapment matrix and its capacity as a sensing element material for assessing various analytes, according to a various studies. In the subject of biosensors, instrumentation is essentially divided into two types. To begin, sophisticated, high-throughput laboratory devices capable of measuring complex biological interactions and components quickly, precisely, and conveniently. Next, simple, portable devices for decentralized, in situ, or at home analysis by nonspecialists.

Clark and Lyons' groundbreaking description of an "enzyme electrode" outlined the fundamental notion of the biosensor for the first time [25]. By combining the advantages of high conductivity associated with polyaniline and the wide surface area of the ordered mesoporous shape, a mediator-free H₂O₂ biosensor with enhanced sensor response and linearity has been developed [26]. Polyaniline is an effective conducting substrate for sensor and biosensor construction due to its adept redox behaviour and ability to facilitate electron shuttling between the reaction site and the electrode surface via biomolecules (in biosensors). Polyaniline's presence of two redox couples at the appropriate electrochemical potential promotes enzyme–polymer charge transfer activities, making it an excellent choice for electrochemical biosensor development. [27].

Example of biosensor that applied polyaniline as the base are glucose biosensor, cholesterol biosensor, DNA biosensor, immunosensors, polyaniline-based phenol, polyphenol, and catecholamine biosensors and others. Polyaniline has also been examined as a basis for developing amperometric biosensors to detect a variety of other critical and therapeutically significant analytes such as urea, uric acid, creatinine, amino acids, pesticides, and so on. During the process, the polyaniline will mediated the electron transfer process from the biochemical reaction site to the electrode surface for electrochemical biosensors [25].

5 Conclusion
Although there were many advance biomedical applications technology, the fact is conjugated polymer like polyaniline could become more interesting to study therefore it is the only polymer that can be controlled in a reversible manner in electronic structure. The simplest doping and dedoping of the polyaniline make it more unique compare to the others polymer. Polyaniline has been used in many biomedical applications because of its high conductivity and stability in the environment.

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