Wearable Flexible pH sensor for biomedical applications

by

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Capteur de pH chimérique flexible portable basé sur un nanocomposite de polyaniline / nanotube de carbone pour les applications biomédicales

Homa Emami

RÉSUMÉ

Dans ce projet, un capteur chimiorésistif flexible sérigraphié à base de polyaniline sel d'émeraldine (PANI (ES)) et de nanotubes de carbone à paroi simple (SWCNT) sur des substrats PET est présenté. Les bandages intelligents avec capteurs intégrés peuvent aider à déterminer la santé des cellules tissulaires endommagées et l'état du bandage lui-même en détectant le pH de l'analyte fluide de la plaie. L'un des paramètres les plus importants qui modifie les plaies dans différents états est le pH et pourrait aider à apporter une valeur ajoutée aux patients et aux agents de santé dans l'identification du début de l'infection Les capteurs chimiques fonctionnent en présence d'une cible chimique basée sur des changements électriques de résistance. Une solution optimisée de solution SWCNTs/PANI (ES) (60/40 % en poids) a été coulée par goutte sur des électrodes d'argent flexibles sérigraphiées sur un substrat de polyéthylène téréphtalate. Le capteur a été recuit à une température optimisée de 90 °C pendant 1 heure avec une étape ultérieure de drop-cast et de recuit PANI (ES). Le capteur de pH chimiorésistif développé a atteint une stabilité de signal élevée, une sensibilité de 2,72 /pH, une linéarité dans la plage de pH de 2 à 10 et des temps de réponse de 70 secondes. La sensibilité du pH du nanocomposite SWCNTs/PANI dépend du processus de protonation/déprotonation. En utilisant des méthodes de fabrication électronique imprimées, nous pouvons développer des capteurs chimirésistifs qui seront un élément clé de notre système de pansement médical intelligent. Ils ont également le potentiel pour différentes applications telles que; l'agriculture, les industries, l'emballage alimentaire et la surveillance de l'eau.

Mots-clés: Capteurs pH, capteurs pH chimirésistifs, sérigraphie, pansements intelligents

Wearable Flexible pH sensor for biomedical applications

Homa Emami

ABSTRACT

In this project, a screen-printed flexible chemiresistive sensor based on polyaniline emeraldine salt (PANI (ES)) and single-walled carbon nanotubes (SWCNT) on PET substrates is presented. Smart Bandages with embedded sensors can help determine the health of damaged tissue cells and the status of the bandage itself by detecting the pH of the fluid analyte from the wound. One of the most important parameters that changes in wounds in different states is pH, which could help bring added value to patients and health actioners in identifying the onset of infection. Chemiresistive sensors operate in the presence of a chemical target based on electrical changes in resistance. An optimised solution of SWCNTs/PANI (ES) (60/40 wt%) solution was drop-casted on top of flexible silver electrodes screen-printed on a polyethylene terephthalate substrate. The sensor was annealed at an optimised temperature of 90 C for 1 hour with a subsequent PANI (ES) drop-casted and annealing step. The developed chemiresistive pH sensor achieved high signal stability, sensitivity of 2.72 pH, linearity in the pH range of 2–10, and response times of 70 seconds. The pH sensitivity of the SWCNTs/PANI nanocomposite depends on the protonation/deprotonation process. The chemiresistive sensor can monitor the changes in the resistance of nanocomposite films (SWCNT, PANI) in different ranges of pH. By using printed electronic fabrication methods, we can develop chemiresistive sensors, which will be a key component of our smart medical bandage system. They also have the potential for different applications, such as agriculture, industries, food packaging, and water monitoring.

Keywords: pH sensors, chemiresistive pH sensors, screen-printing, smart bandages

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LIST OF ABBREVIATIONS

CNT	carbon nanotube
SWCNT	Single wall carbon nanotube
MWCNT	Multi wall carbon nanotube
DWCNT	Double-walled
PANI	Poly aniline
PANI (ES)	poly aniline(emeraldine salt)
PANI (EB)	Emeraldine base (EB; half oxidized form)
PANI(PNB)	Pernigraniline base
ISFET	Ion Sensitive Field Effect Transistor
EMF	Electromotive force
EGFETs	Extended-gate field-effect transistors
RE	Reference electrode
SDS	Sodium dodecyl sulfate
PET	polyethylene terephthalate
NMP	N- methyl-2-pyrrolidone
SEM	Scanning Electron Microscopy
IoT	Internet of things

LIST OF SYMBOLS AND UNITS OF MEASUREMENTS

O_2	Oxygen Atom
H^+	Hydrogen ion
Ag	Silver
AgCl	Silver chloride
MOx	Metal oxides
RuO_2	Ruthenium oxide
IrO_2	Iridium oxide
TiO_2	Titanium dioxide
ZnO	Zinc oxide
RuO_2	Ruthenium oxide
MnO_2	Manganese oxide

INTRODUCTION

pH sensors are widely used in numerous applications such as food packaging, biological sensing, water quality monitoring, agriculture optimization, environmental remediation, and medical diagnosis (Gu, Yin, Zhang, Qian & He, 2011)-(Manjakkal, Sakthivel, Gopalakrishnan & Dahiya, 2018). In the field of biomedical processes; pH sensor is an effective element in the blood test, diagnosis of cancer, and tissue problems (Granja, Tavares-Valente, Queiros & Baltazar, 2017). In particular, smart bandages by using different types of sensors such as; humidity, temperature, and pH sensors can detect the status of the skin and the bandage itself. These are the factors that alter after the appearance of a chronic wound on the skin. pH sensor measures the pH level of the skin when affected by a chronic wound. pH sensor measures the pH level by detecting the fluid coming out of the chronic wound (Farooqui & Shamim, 2016). The pH level of the normal skin is acidic and between 4 to 6. As the increase in pH level is one of the important signs of skin infection, a pH sensor can be vital in detecting the onset of infection (Ali & Yosipovitch, 2013a). According to the severity of infection which is characterized by the pH level measured by the pH sensor, the smart bandage can determine the state of the skin and the bandage.

The purpose of this study is to design and fabricate a pH sensor to be used in the smart bandages system. This pH sensor should have some features such as; flexibility, wearability, short response time, ease to fabricate, high signal stability, small size, and high sensitivity.

Throughout the research we have faced with following questions:

- What is the best design?
- What are the right materials?
- What are the best dimensions to have a small size of pH sensor?
- What is the best technique to fabricate the pH sensor?

In the first chapter, we will have an overview on smart bandages and their application in wound healing by detecting the important parameters and answering the question of why pH sensing is an important part of smart bandages.

In the second chapter, we reviewed the pH description, different existing pH meters, different applications of pH measurements, and the reasons for fabricating the chemiresistive pH sensor.

In the third chapter, hydrogen-sensitive materials, their advantages, disadvantages were reviewed. In this chapter we went through the details of PANI, CNT, all the materials and their preparation methods which were used in our project.

In the fourth chapter, the most common pH sensor fabrication techniques, their fabrication process, and their limitation were reviewed. We explained about screen printing and its benefits for our project. We also explained the fabrication process, preparation and design of our chemiresistive pH sensor.

In the fifth chapter, the results of testing our chemiresistive pH sensor in different pH levels were provided and we will discuss about each result and different approaches.

0.0.1 Publications

Two published conference papers related to this thesis:

Emami, H., Mahinnezhad, S., Al Shboul, A., Ketabi, M., Shih, A. Izquierdo, R. (2021). Flexible Chemiresistive pH Sensor Based on Polyaniline/Carbon Nanotube Nanocomposite for IoT Applications. 2021 IEEE Sensors, pp. 1–4

Mahinnezhad, S., Emami, H., Ketabi, M., Al Shboul, A., Belkhamssa, N., Shih, A. Izquierdo, R. (2021). Fully Printed pH Sensor Based in Carbon Black/Polyaniline Nanocomposite. 2021 IEEE Sen- sors, pp. 1–4

CHAPTER 1

SMART BANDAGE

1.1 Introduction

Chronic wound healing has changed significantly in recent years. Wounds are defined as lesions and fractures of the skin surface caused by physical or heat injuries that require medical treatment. Wound healing in humans and evolved animals with a complex and advanced mechanism happens as the result of going through various stages such as inflammation, proliferation, repair, and regeneration.

Researchers have developed a flexible bandage that actively monitors chronic wounds and then responds by providing specific wound healing treatments. This can be a significant improvement for people with chronic skin wounds that are difficult to treat, such as burns or diabetes. In the near future, chronic wounds will be treated with smart electronic bandages for real-time treatment and delivery of medicine.

In this chapter, wounds and wound healing is elaborated on in detail, then all existing bandages are classified and explained. Afterward, the smart bandages are categorized into various groups and their associated characteristics are provided in great detail.

1.2 Wound

The Wound Healing Association defines a more precise definition as "destruction of the anatomical and functional structure of the skin" for a wound. Based on its nature, the wound healing process can be divided into acute and chronic wounds. Acute wounds are a group of wounds that are usually superficial and heal completely in 8 to 12 weeks, while chronic wounds last more than 12 weeks. (Ghaderi *et al.*, 2010).

1.2.1 Wound healing

The wound healing stages are demonstrated in figure 1.1 :

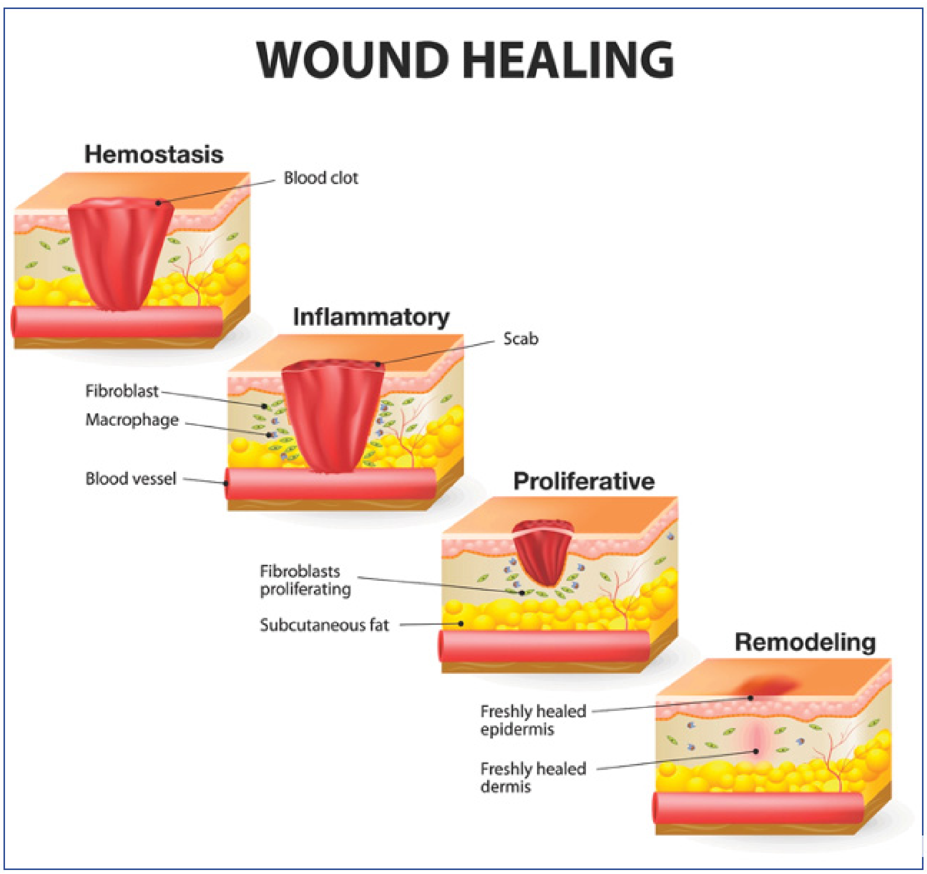

Figure 1.1 Wound healing stages natural.breast.reconstruction

The wound healing stages are listed below (Pinto, Cerqueira, Bañobre-Lópes, Pastrana & Sillankorva, 2020) :

1. **Hemostasis**:

   In this phase, first the arteries constrict and platelet damage activates the coagulation process, followed by fibrin formation. Under the influence of complement and prostaglandin components, small, localized arteries dilate and plasma proteins and white blood cells enter the wound. This causes a clot which is able to close the gap in the blood vessel, slowing it down and preventing further bleeding.

2. **Inflammatory**:

   Macrophages are the most important cells in completing the inflammatory phase that secrete several growth factors, which stimulate the fibroblasts themselves and the epithelial and endothelial cells to heal the wound.

3. **Proliferation**:

   This phase includes: formation of new blood vessels, proliferation of fibroblasts and it is made of epithelium.

4. **Remodeling**:

   This phase begins quickly and lasts for months. At this stage, collagen production is done by fibroblasts and stimulated by macrophages. Accumulation and placement of collagen and other cellular matrix proteins give the repaired tissue strength and power. Within 10 hours of injury, evidence of collagen increase becomes apparent, which peaks after 5-7 days and then gradually decreases; finally, the production of collagen fibers in wound healing increases the tensile force in the new tissue created at the site of healing. Disruption of any of the repair steps can lead to infection, non-healing of the wound, or eventually atrophic or hypertrophic scars.

   As it is obvious in the figure 1.2 pH is a parameter which is started to be changed right immediately after injury. First, we can see a sever drop in the pH level. In the middle of the first stage of wound healing process, inflammation, pH level begins to increase. At the end of the third stage, proliferation, pH level starts to decrease and the end of the fourth stage, pH level returns to normal level of before injury.

Since pH is parameter changes during the healing process stages, By detecting the level of pH constantly, we can predict and monitor the wound state after injury and during healing process.

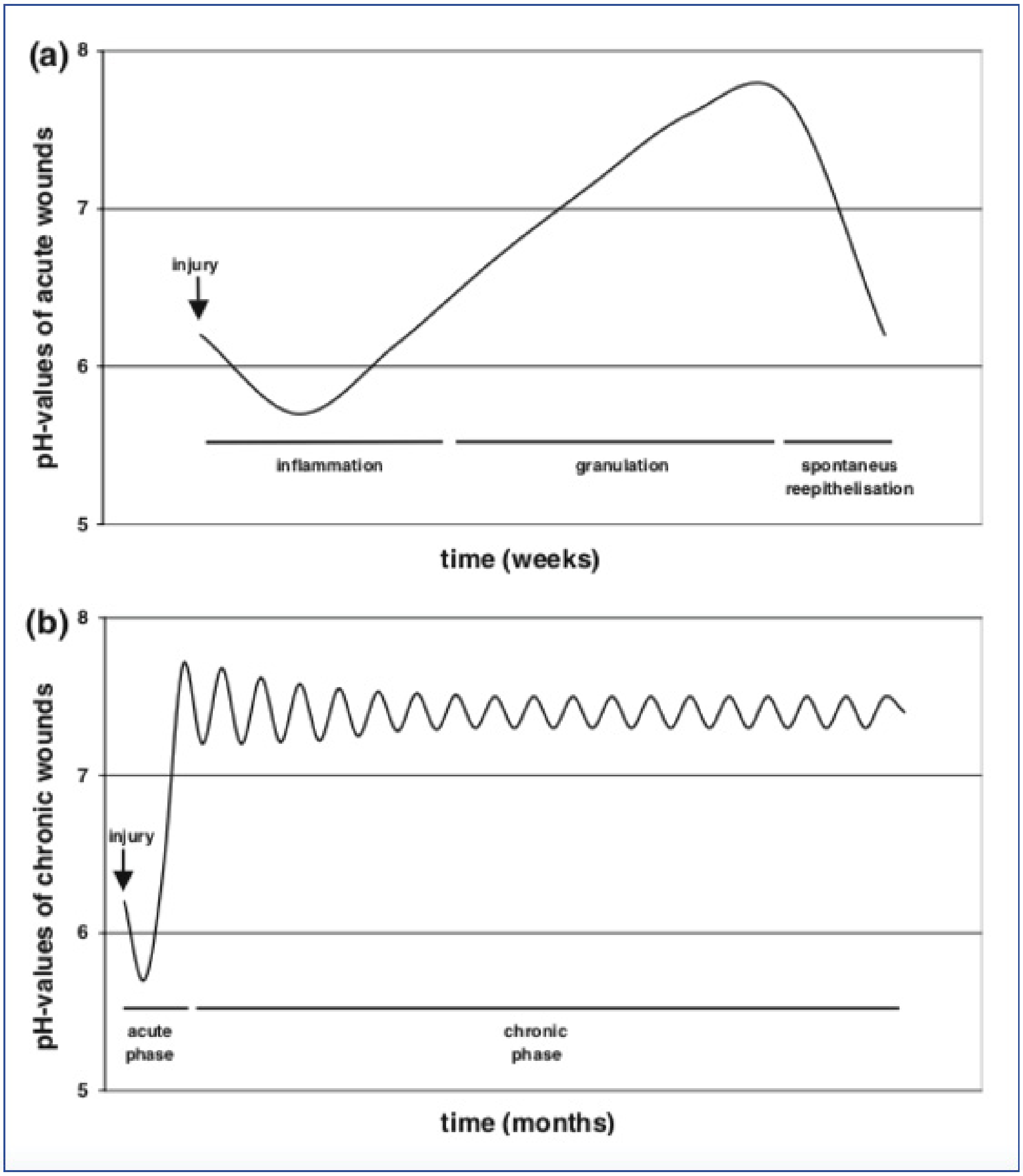

Figure 1.2 pH Changes in Wound healing stages Schneider *et al.* (2007b)

1.3 Bandage Classification

Choosing the right bandage, along with other treatments, is of particular importance in wound healing management. A bandage should be designed to be suitable for different stages of wound healing; be non-sticky; be permeable to air and can pass secretion and does not cause allergies; be sterile; allow gas exchange; it has a high absorption rate and maintains proper temperature and in general, provides the best conditions for wound healing. (Derakhshandeh, Kashaf, Aghabaglou, Ghanavati & Tamayol, 2018a). Bandages are divided into two categories:

1.3.1 Traditional bandages

The traditional bandages are categorized as (wound.care.uk):

1. **Gauze pad:** Gauze pad is made of linen with paraffin, which is permeable to air and can pass secretions. Grasolind does not cause allergies. The fibers of this pad are woven and integrated and do not leave any lint or residue in the wound. This dressing is sterile and available in separate packaging.
2. **Silver pad:** This dressing consists of a hydrophobic and silver-plated polyamide network impregnated with plant-specific triglyceride neutral fats.
3. **Atrauman , a gauze pad impregnated with vegetable fats:** Atroman is made of hydrophobic polyester and a mesh that is impregnated with vegetable fats. This dressing is free of paraffin, vaseline and oil derivatives and is very compatible with the skin.

Although these bandages have advantages, they can not provide information such as diagnostic and infection. With these traditional bandages, the healing process would be much longer and it can increase the need for the presence of nurses and doctors. Increasing healthcare costs for patients and insurance providers. Smart bandages by detecting the important parameters of wounds with embedded sensors can state the wound and decrease healthcare costs.

1.4 Smart Bandage

Treating wounds that are difficult to heal can be very challenging. Emerging therapeutic technologies that are entering the field could change the way wound care is performed. At present, the evaluation and monitoring of wound care is practically entirely subjective and may vary between physicians. Visual inspection and manual measurement are commonly used to assess wound progression. Wound inspections typically require removal of the dressing and may result in excessive dressing changes, increased clinical inspection time, patient discomfort, and increased cost of wasted dressings. Physicians may use laboratory cultures, biopsies, and other laboratory tests when necessary, but processing these steps is time consuming and may delay treatment. So it makes sense that a more active method of wound assessment that can provide physicians with slightly better data in a timely manner would be very helpful. In the near future, a number of smart banding options can do it (Mostafalu *et al.*, 2018b). figure 1.3

The whole bandage structure is attached to a transparent medical adhesive. Forms a flexible bandage with a diameter of less than 3 mm. With the exception of the microprocessor, parts for this bandage have been used that are cheap and disposable.

This electronic bandage can treat old wounds caused by burns, diabetes and other health conditions. These old wounds cost a lot of money each year to heal. 6.5milion people in USA effected by chronic wounds and it costs up to 25 bilion dollar to heal them. Smart bandages can provide the right treatment with minimal patient or nurse interference. Bandages can also help the skin's natural healing process with the help of a range of different sensors (McLister, McHugh, Cundell & Davis, 2016).

Electronic bandages are defined as a subset of smart clothing. These flexible electronic components also make the production of wearable medical gadgets easier. Although many products have been tested in this field, it seems that this product can greatly increase the likelihood of using electronic devices in the body. The next step in upgrading this bandage is to set up a remote warning system. This system sends the doctor warnings about the need for intensive wound care.

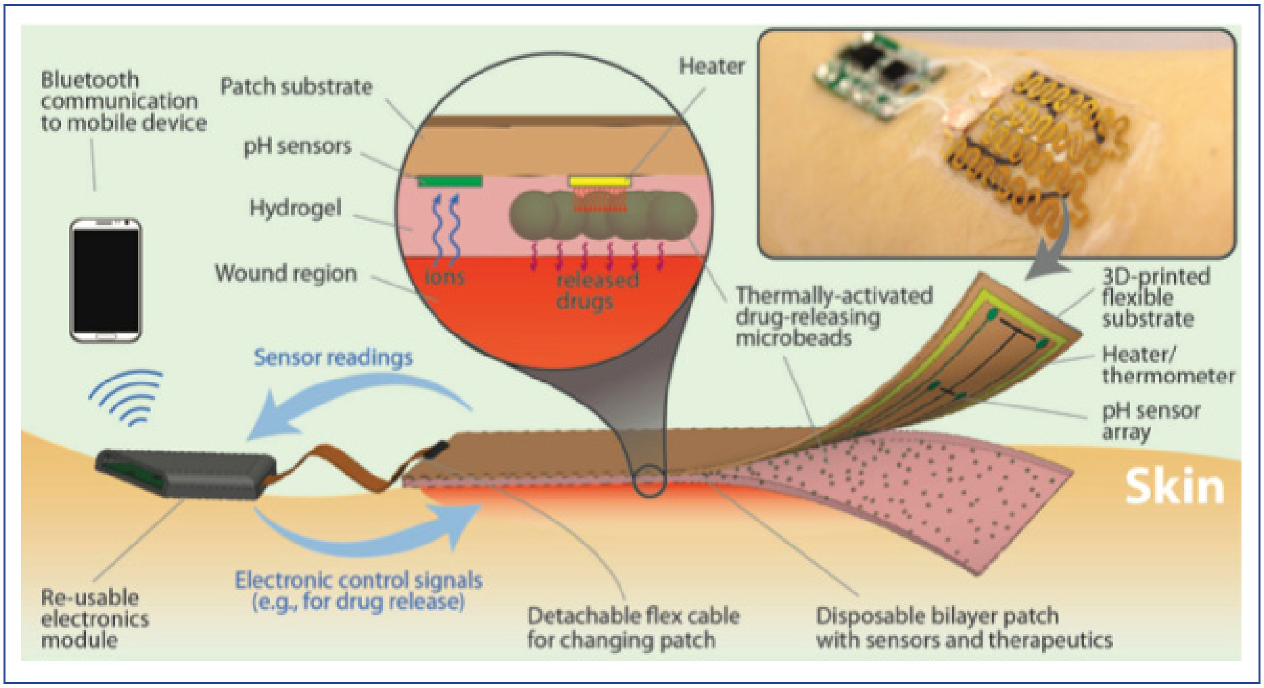

Figure 1.3 How the smart bandage collects wound data, then delivers medications and communicates with a mobile device Mostafalu *et al.* (2018b)

The bandage will be equipped with a nano-sensor and will transmit patient information to the medical center remotely. The patient is then instructed to continue the treatment remotely so that the wound healing period can be completed sooner (Mostafalu *et al.*, 2018b).

This bandage directs the health monitoring system through the remote communication infrastructure to the user's mobile phone or the desired health center and through the defined application.

The expected function of standard bandage materials is to provide a moist environment for wound healing and to promote wound healing while protecting against contamination. A smart bandage can do these functions plus much more. Research is currently underway on several different bandaging systems, including embedded sensors, that can wirelessly transmit various valuable wound parameters. These products can independently monitor both the condition of the wound and the dressing itself. This information gives physicians a real-time insight into the wound environment and helps facilitate more effective and personal wound care treatments. Some of the specific wound parameters that can be potentially monitored are listed below (Derakhshandeh *et al.*, 2018b):

1.4.0.1 Temperature

Most cellular functions are affected by temperature. Rising and prolonged body temperature in a chronic wound can indicate inflammation and signs of a bacterial infection. If Micro-fabricated metallic resistive sensors can be incorporated into intelligent bandaging systems for continuous wound temperature monitoring, it may act as a rapid method for detecting wound infection. Function and fabrication process of a temperature sensor is depicted in figure **??**

1.4.0.2 Oxygenation

Oxygen plays a key role in all stages of wound healing. Without adequate oxygen levels, wound healing is impaired. Studies have shown that the partial pressure of O_2 in non-healing wound secretions is 5 to 20 mm Hg compared to 30 to 50 mm Hg seen in healthy tissues. Smart dressings that can control skin oxygen have real potential applications in wearable dressings. figure. 1.5 shows oxygen consumption in the wounded skin and healthy skin.

1.4.0.3 Moisture

Keeping the wound moist makes the wound healing process much faster by reducing the inflammation and improving the proliferative stage of dermal repair. It is shown that the there is a greater rate of revascularization in moist environment. Moreover, it is found that dry wounds have a slower progression to the remodeling phase of wound healing. However, extra leakage from bandage may cause the risk of bacterial infection due to the moist environment.

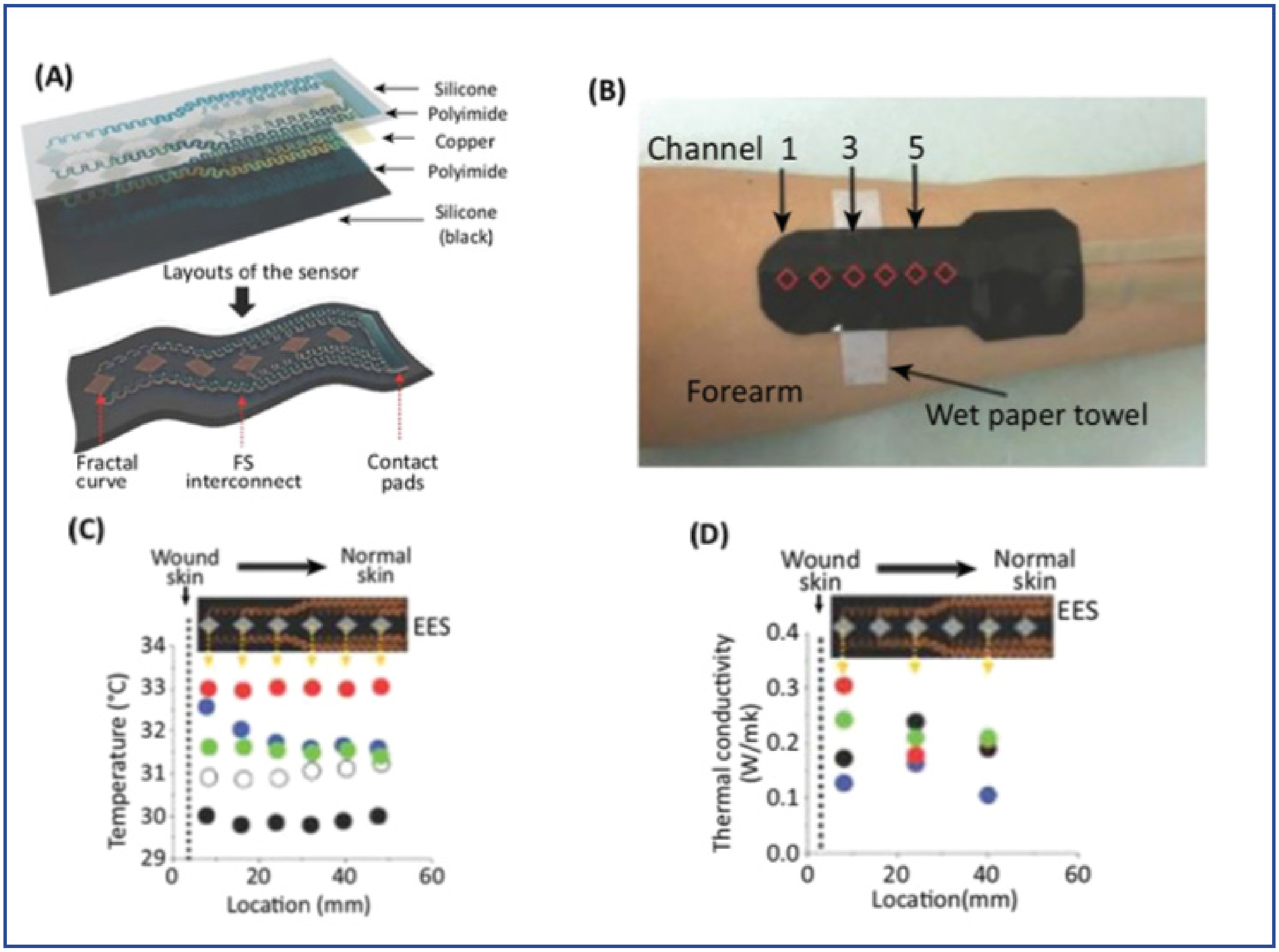

Figure 1.4 (A) fabrication process of a temperature sensor. (B) bandages containing temperature sensor contacts with skin. (C,D) Temperature and thermal conductivity measured by temperature sensor Derakhshandeh *et al.* (2018b).

1.4.0.4 Enzyme

The level of enzyme such as upregulations of cathepsin G and elastase is suggested as a good indicator for the level of infection.

1.4.0.5 Mechanical and Electrical

According to the simulation of mechanical and electrical property of a wound, it is shown that these two characteristics can facilitate wound healing process and prevent infection. Therefore,

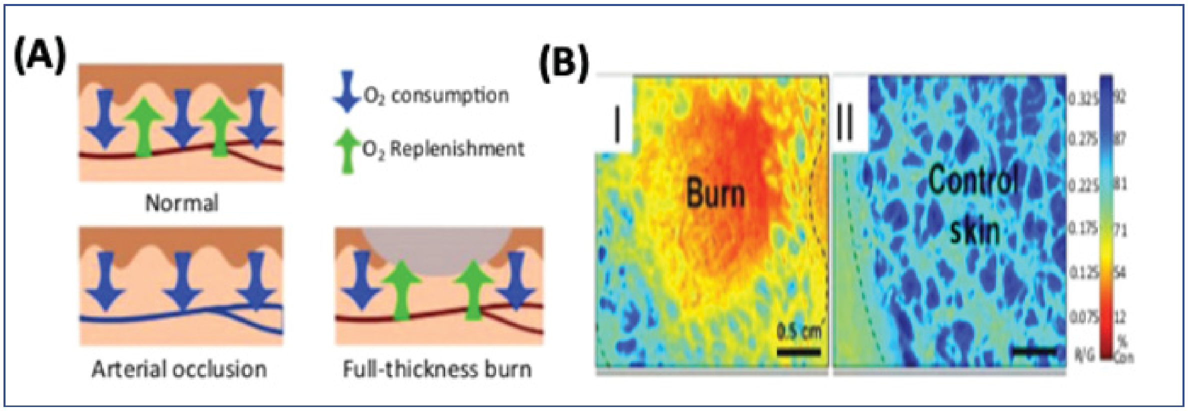

Figure 1.5 (A) O_2 consumption in the tissue. (B)red parts consumes lower oxygen than the red parts Derakhshandeh *et al.* (2018b).

one can obtain important information about tissue condition through the sensors which are able to measure the stiffness and impedance of the skin.

1.4.0.6 pH

Various factors affect skin pH:

- Pimples and acne
- Antibacterial products
- changing weather conditions
- Use of cosmetics
- Use detergents with unbalanced pH
- Use of soaps and antibacterial gels with unbalanced pH
- Sweat
- Age
- Excessive sun exposure
- essive and frequent washing of the skin

pH plays an important role in wound healing. Measuring the pH level can play an important role in the early detection of non-healing wounds. Healing wounds tend to operate in a slightly acidic environment, usually in the pH range of 5 to 6. In contrast, wounds that are difficult to treat or chronic have a pH of 7 to 9. This is thought to be due in part to increased bacterial levels. Therefore, large changes in pH can be an early warning sign of the possibility of wound infection.The skin barrier is acidic because it can retain moisture and prevent bacteria from entering. If your skin's pH balance is upset and it becomes too alkaline, it will look flaky and red. If it becomes too acidic, more likely to develop inflammatory skin conditions such as eczema, acne and wounds (Schneider, Korber, Grabbe & Dissemond, 2007a).

1.5 conclusion

When the skin is becoming wounded, as we reviewed in this chapter, in addition to going through 4 steps to regenerate skin tissue, several parameters change in the skin, such as moisture, pH, temperature, and enzymes. Older traditional bandages, while having benefits and protecting the skin from bacterial contamination to some extent, are not able to predict changes in the parameters of the injured skin. Smart bandages with embedded sensors can collect data about these parameters and assess the stage of the wound healing process. they can also assess the state of the bandage itself. Shortly, these bandages can do drug delivery and reduce the cost of wound healing.

CHAPTER 2

STATE OF THE ART IN PH SENSOR MEASUREMENT

2.1 pH Description

pH of a solution is the concentration of hydrogen ions dissolved in it, expressed by a scale under this heading. pH determines the degree of acidity or alkalinity of a substance or solution and is measured on a scale of 0 to 14. pH is the most common analytical assessment in industrial processes and plays a very important role in various industries such as agriculture, food, health system (pH.description).

7 pH is considered neutral, values less than that are acidic and values above 7 are considered alkaline pH. pH is actually a term that refers to acid and base. An acid is a substance that releases hydrogen ions when dissolved in water. Acids are mostly sour in taste and most foods have an acidic pH (pH.description).

Based on the pH scale, substances with a pH below 7 are considered acidic and substances with a pH above 7 are considered alkaline.

Examples of edible acids include vinegar, lemon juice, carbonated beverages, juice or orange and tomato juice, and familiar bases of soap, bleach, and seawater.

pH is the negative logarithm of the concentration of hydrogen ions (Ogston, 1947):

$$pH = -\log([H^+]) \tag{2.1}$$

Due to the logarithmic nature of pH, even small changes in pH are significant. In fact, the difference between pH 6 and pH 5 indicates a 10 times increase in acid concentration (whoi.edu). It is worth noting that a change of only 0.3 indicates a doubling of the acid concentration. pH changes can affect the taste, consistency and shelf life of food.

2.2 Available pH Detectors

pH meter is a scientific tool and one of the laboratory equipment required in various laboratories to measure hydrogen-ion activity in various solutions. Commercial pH meter is an electrical device and one of the most important laboratory equipment that is always used to calculate and measure the pH of samples to detect whether the material is acidic or alkaline.

2.2.1 pH strip papers

As it is shown in figure 2.1 pH strip paper is a laboratory device used to test whether a substance is acidic or alkaline. When a substance dissolves in water, the resulting solution changes the color of the paper. The acidity or alkalinity of a solution is determined by the concentration of hydrogen ions or the strength of the hydrogen, expressed as the pH value. The test gives a quick result but cannot determine the accurate level of acidity or alkalinity of the solution (Duggan, Smyth, Egan, Roddy & Conlon, 2008).

It is a quick and easy way, but it suffers from some limitations. First, it is not an accurate indicator for pH. It does not set the pH value as a accurate number. Instead, it indicates that the sample is almost acidic or alkaline. Second, it can discolor for reasons other than the base/acid reaction (chrominfo.blogspot).

2.2.2 Glass micro-electrode pH meter

Glass electrodes are considered as membrane detection electrodes. These electrodes are sensitive to different ions. For example, a pH electrode is an electrode that is sensitive to the concentration of H^+ ions. The electrode consists of a glass bubble whose bottom is about 0.1 mm or less thick and it has a shape like a bubble. A solution with a specific pH is poured into the bubble and a reference electrode such as a silver-silver electrode and AgCl covered silver wire is inserted into the solution. Inside of the electrode usually filled by a buffer solution such as chloride. This set and another control electrode are dipped into a solution which pH must be determined as we can see in figure 2.2 (Carter & Pucacco, 1978).

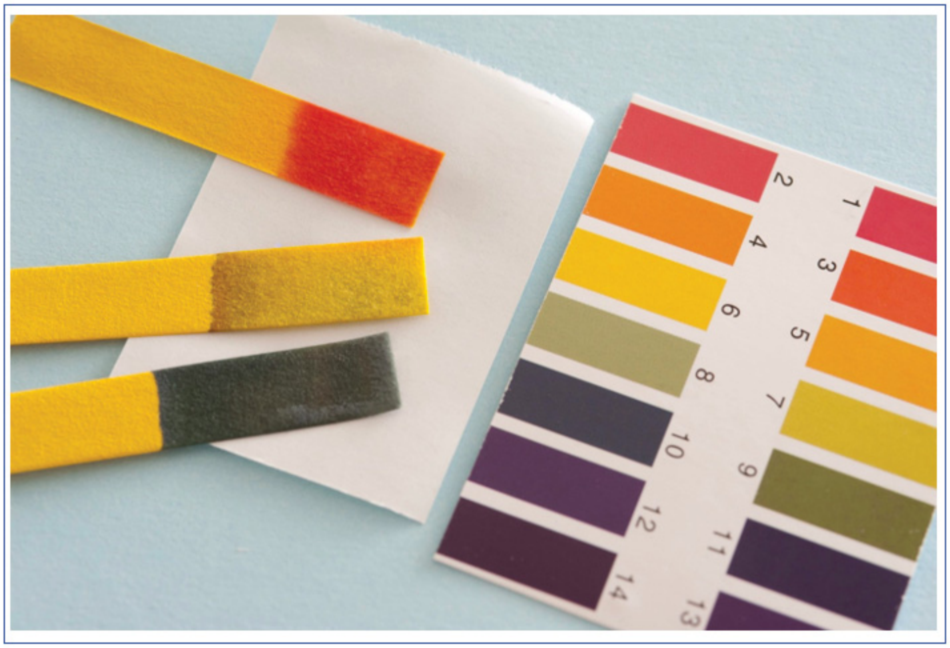

Figure 2.1 pH strip paper.

2.2.2.1 Function of glass micro-electrodes

After dipping the glass electrode in the sample solution to detect the pH level, Potential is generated throughout the glass membrane due to the difference of H^+ ions on both sides of the membrane.

Detecting the pH level of a sample solution is based on the changes in the potential of the glass. the behaviour of the glass electrode is described by the Nernst equation (qsstudy):

$$EGlass = E0Glass - (RT/F)ln[H^+] = E0Glass - 0.0591pH \tag{2.2}$$

The glass electrode combined with the calomel electrode, the EMF of the cell provided by:

$$Ecell = Ecal - EGlass \tag{2.3}$$

$$Ecell = Ecal - EGlass - 0.0591pH \tag{2.4}$$

then:

$$pH = (Ecal - EGlass - Ecell)/0.0591 \tag{2.5}$$

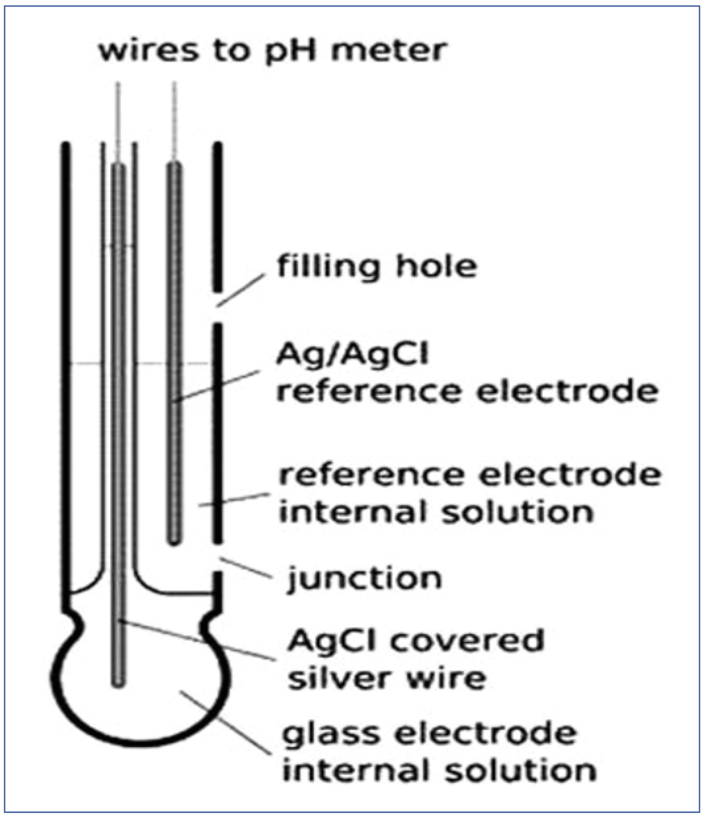

Figure 2.2 Glass pH meter acsedu

2.2.3 Electronic based pH Meter

One of the important devices for pH level detection is ion-sensitive field-effect transistor (ISFET) shown in 2.3 which measures the concentration of the Ions in a solution such as H^+ which is a sign for pH level measurements. A structure of field-effect transistor contains two semiconductor electrodes, drain and source electrodes. These two electrodes are in a silicon chip. A third electrode, gate, placed between them. Gate electrode is a part of field-effect transistor which directly contacts to sample solution (Rani & Sidek, 2004).

2.2.3.1 Function of ISFET

The function of ISFET is based on monitoring the current flowing between two semiconductor electrodes. The gate electrode is the sensitives part of the field-effect transistor and contains hydrogen sensitive material such as silicon oxide (SiO2), silicon nitride (Si3N4) and aluminium oxide. When the sensitive part of the transistor contacts to a sample solution, hydrogen ions absorbed by the transistor and effects on the current between drain and source electrode. So the the pH level of a solution can change the current flow. A control voltage is applied by the reference electrode to balance the current between drain and source electrode. Measuring the pH level is based on the changes in the control voltag. Similar to the glass electrodes the Nernst equation justifies the behaviour of Field-effect transistors (Rani & Sidek, 2004).

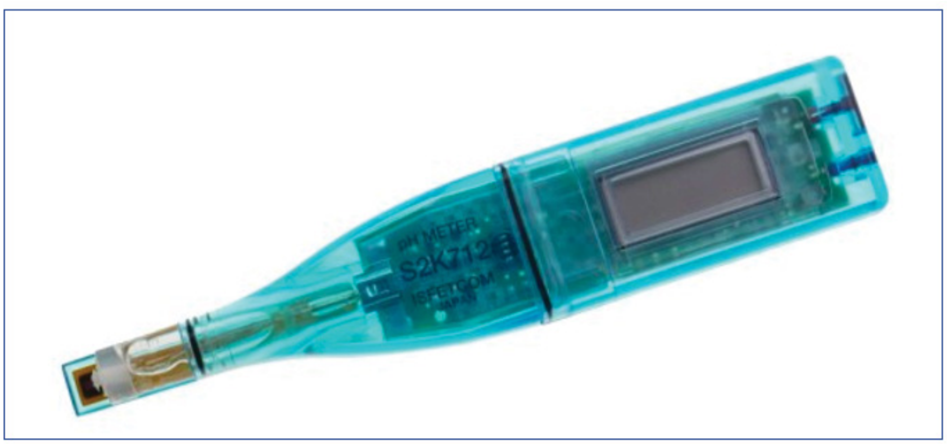

Figure 2.3 ISFET pH meter Deltatrak

2.2.4 Potentiometric pH sensor

Potentiometry is one of the most popular techniques used to fabricate printed pH sensors embedded in flexible and stretchable devices. In contrast with glass electrodes, the device structure of solid-state potentiometric sensors are simple, and the fabrication process is cost effective (Mahinnezhad *et al.*, 2021). Its presented in figure 2.4

2.2.4.1 Function of potentiometric sensor

The potentiometric pH sensor works on the basis of the generation of an electromotive force (EMF) difference between a pH sensitive working electrode and a reference electrode. The reference electrode can be made from Ag/AgCl which is one of the most commonly used materials due to its low environmental impact and its great potential stability. The pH sensing materials typically involve conducting polymers and metal oxides. Potentiometric pH sensor require a reference electrode that limits their size (Mahinnezhad *et al.*, 2021).

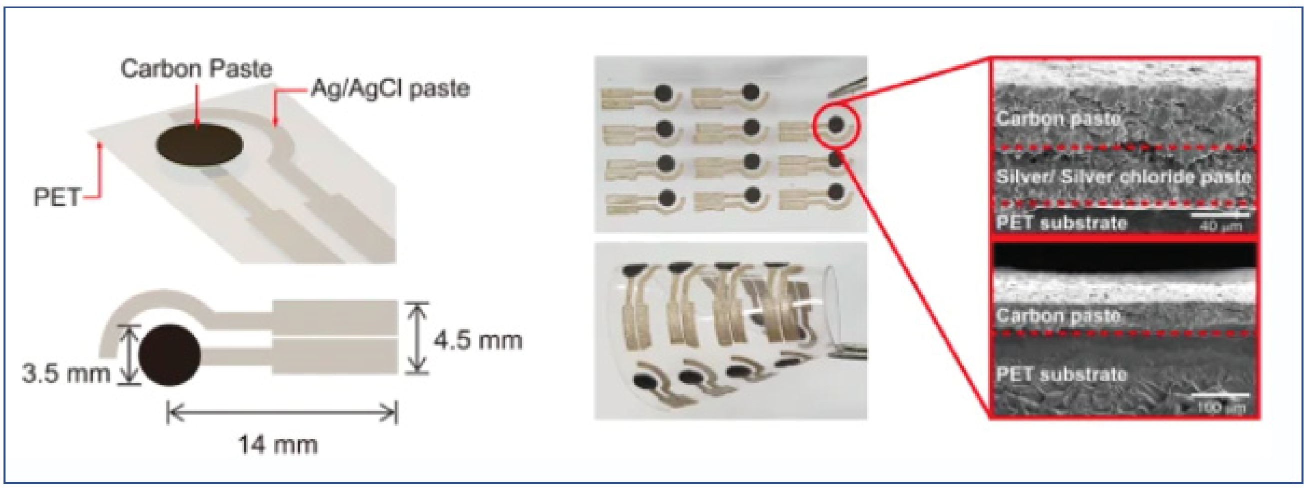

Figure 2.4 schematic of potentiometric pH sensor fabrication process Park *et al.* (2019)

2.2.5 Comparison between existing pH meters

- **pH strip paper**
  - advantage: Cheap, Quick and easy to use
  - disadvantage: Does not indicate accurate number, effected by other materials
- **Glass micro-electrode**
  - advantage: High accuracy
  - disadvantage: Can not be bent, needs refrence electrode, expensive

- **ISFET**
  - advantage: Good response time
  - disadvantage: Needs reference electrode, very expensive
- **Potentiometric pH sensor**
  - advantage: High stability, flexible
  - disadvantage: Needs reference electrode

2.2.6 Chemiresistive pH sensor

One of the most important devices for detecting the pH level are Chemiresistive pH sensors. These kinds of sensors are easy to fabricate and cost effective. like the sensors we explained before, ISFET and glass micro-electrode, chemiresistive pH sensors does not require a reference electrode and does not need to measure the EMF (Emami *et al.*, 2021).

2.2.6.1 Function of chemiresistive pH sensor

Chemiresistive pH sensors Work based on the changes on the electrical resistances between two conductive electrodes through absorption of ions on the surface of the conductive or semi-conductive material on the surface of the electrodes as shown in figure 2.5. Changes in the electrical properties depends on the protonation and deprotonation that occurs due to the de-doping and doping of the active material in the device. After exposing the sensor in the acidic solutions the hydrogen sensitive material between the electrodes absorbs hydrogen ions in the sample solution and caused by increased conductivity, resulting in decrease the the electrical resistance between the electrodes. The electrodes can be fabricated of specific material such as carbon or silver which is covered by a sensitive material to hydrogen ions such as metal oxides, carbon nanotubes, polyaniline (Emami *et al.*, 2021).

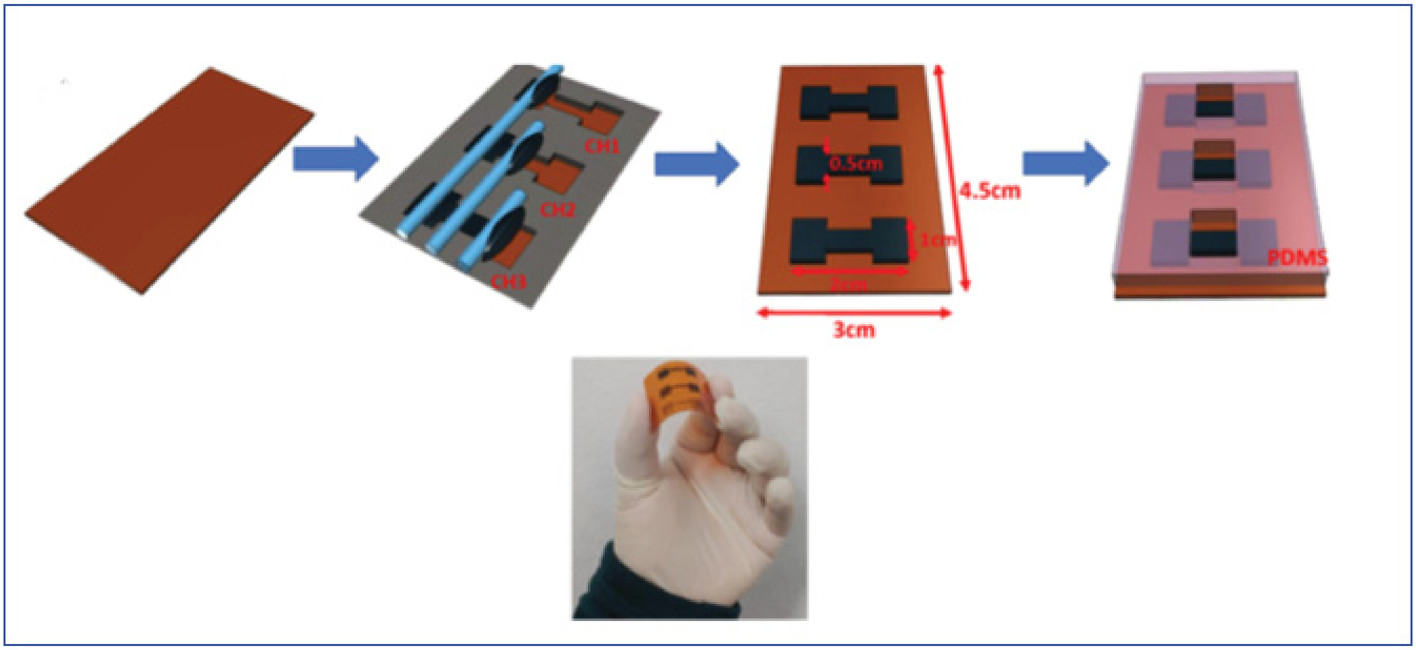

Figure 2.5 chemiresistive pH sensor using SWCNT as an active material Jeon *et al.* (2020b)

2.3 Advantages of fabricated chemiresistive pH sensor

Commercial glass microelectrodes can measure skin pH. However, their real-time therapeutic effectiveness is diminished as they are brittle and cannot measure the pH value at multiple points. Furthermore, the leakage of electrolytes impacts its efficiency. Alternative options have been presented such as ion-selective field-effect transistors (ISFETs) and the potentiometric pH sensor. However, they both require a reference electrode that limits their size. Metal oxides are also used as hydrogen-sensitive material in extended-gate field-effect transistors (EGFETs). Nevertheless, the use of metal oxides negatively affects the mechanical stability of fabricated. Sensors resulting in fragile sensors. Chemiresistive pH sensor is a optimal option for smart bandages because they can be bent and printed on flexible substrates rather than sensors that are brittle and printed on a glass surfaces. In addition, these sensors measure electrical parameters more easily because they do not require electrode reference (Emami *et al.*, 2021).

2.4 Application of pH measurement

In various industries such as food, pharmaceutical, medicine and pharmacy, agriculture and animal husbandry and refineries, measuring the acidity of liquids is of special importance, which is measured today by pH meters.

2.4.1 Value of pH detection in environmental resource

In various industries such as food, pharmaceutical, medicine and pharmacy, agriculture and animal husbandry and refineries, measuring the acidity of liquids is of special importance, which is measured today by pH meters.

2.4.2 Value of pH detection in food industry

Foods that spoil quickly are often moist and have a neutral pH, are not refrigerated, and are sliced or sliced. In contrast, dry, acidic, and refrigerated foods are more resistant to spoilage. Microorganisms usually grow best at neutral pH between 6.6 - 5.5. While most bacteria are inhibited at pH below 4, yeasts and fungi can tolerate low pH levels (acsedu).

Since most foods have the proper pH for the growth of microorganisms such as bacteria, molds and fungi, methods such as heating, drying, pasteurization and especially canning are used to protect food from spoilage (acsedu).

PH can also be used as an indicator to determine the quality of meat in the range of 5.4 to 7.0. PH can be a sign that fresh meat is properly stored. For example, higher level of pH destroys the aroma and darkens the meat and reduces its nutritional value. In addition to fresh meat, the pH of ham and sausage can also show the amount of ammonia content in these products (4oakton).

It is worth noting that checking the pH of water before adding it to various food processes provides a quick and easy way to ensure the quality of the final product. As a result, proper pH control in the early stages can have a negative impact on the consistency of the final product (acsedu).

pH plays an important role in the processing of all foods, measuring a constant pH and adding buffering agents control intangible changes in foods and ensure their health.

2.4.3 Value of pH detection in agriculture industry

The purpose of pH adjustment is directly related to the activity of soil microorganisms. There are two types of microorganisms active in the soil, one of which is aerobic and the other type of anaerobic, of which important fungi can be fungi and bacteria (Gougoulias, Clark & Shaw, 2014). Anaerobic bacteria have the highest growth and development in the range of alkaline pHs, but beneficial and aerobic bacteria in acidic pHs have good growth and activity that release elements, so as the pH moves to alkaline, harmful and destructive microorganisms increase and with decreasing pH The activity of beneficial microorganisms is increased and through this the solubility and absorption of elements will be increased (Msimbira & Smith, 2020).

By producing beneficial organic acids by these organisms, solubility of elements and adsorption occurs and in alkaline environments we will not have solubility and absorption of chemical elements, So plant growth and production will not happen. The above points indicate the importance of pH in plant nutrition (Jacoby, Peukert, Succurro, Koprivova & Kopriva, 2017).

2.4.4 Value of pH detection in body system

Everything we eat and drink affects your pH, including acidic foods that significantly increase your body's pH level. The normal functioning of the body requires both environments, and when this quantity is in balance, the body is at its best. Decreasing or increasing the acidity of the environment can affect the function of all organs of the body. Stored resources, such as bone, are sometimes used to balance the body's environment. Excess acid in body fluids can cause osteoporosis, arthritis, diabetes, stroke, heart disease, MS and cancer. On the other hand, reducing the alkaline environment causes nausea, inflammation and reflux (Schwalfenberg, 2012).

Most meat and dairy products are acidic, while fruits and vegetables are very healthy for the body due to their positive effect on controlling this important part of the blood. Exposure of cells to an acidic environment reduces their function, and as a result, their ability to repair themselves is impaired. This is why premature aging occurs. This problem occurs when cells are unable to receive enough oxygen (Schwalfenberg, 2012).

2.5 Application of pH sensor in Smart bandage

Skin pH is very important because it affects several factors that affect the overall health of the skin. Skin with a pH of less than 5 has been shown to be healthier, more moisturized, and has a stronger defense barrier than skin with a pH above 5.0 (Schneider *et al.*, 2007a).

Our skin is protected by a coating called the "acid mantle". This covering is actually a thin layer on the surface of the stratum corneum (the outermost layer of the skin). The stratum corneum itself is made up of fatty acids, lactic acid, pyrrolidine carboxylic acid and amino acids (Ali & Yosipovitch, 2013a).

The acidic coating of our skin is actually a protective barrier on the surface of the skin that consists of sweat, fat and dead skin cells. This acidic coating is what gives our skin a pH, and its acidity is in the range of 4.0 to 6.0 and its average is 4.7. This coating protects our skin against bacteria, fungi, viruses and environmental pollutants, makes the skin soft and supple, and does virtually everything (Schneider *et al.*, 2007a).

Disrupting the acidic balance of this lovely skin protector can have many side effects and lead to problems such as inflammation, atopic dermatitis, dehydrated or dehydrated skin (skin that is both dry and oily at the same time), Dry skin, skin allergies, and acne. The ability of the acidic coating to maintain the integrity of the skin's moisture barrier (a layer that is generally made of fatty acids that help retain skin moisture) and to protect the microbes (beneficial bacteria that live on our skin) is also important (Ali & Yosipovitch, 2013b).

Smart bandages contain different types of sensors such as pH, humidity and temperature. According to the explanations about the skin pH, One of the important parameter plays a vital role in assessing the state of the wound and wound healing process is pH. pH sensor utilized in smart bandage can detect the pH level and predict the state of the wound (Mostafalu *et al.*, 2018a).

2.6 Conclusion

In this chapter, pH definition and different kinds of available pH meter were reviewed. Since smart bandages requires a pH sensor with important features such as, flexibility, easy to fabricate, cost effective, small size and also easy to do electrical measurements, chemiresistive pH sensor is the best choice for utilizing in smart bandages. Furthermore, the importance of pH and pH detecting in environment, food industry, agriculture and body system was described. Chemiresistive pH sensor with its beneficial features such as being flexible, high accuracy and without reference electrode can be used also in mentioned industries and systems.

CHAPTER 3

HYDROGEN-SENSITIVE MATERIALS AND CONDUCTIVE MATERIALS

3.1 Introduction

There some kinds of chemical materials are utilized in the different types of pH sensors that we mentioned in the previous chapter to detect the hydrogen ions in the sample solution. The most common materials that are used in the in the chemiresistive pH sensors are metal oxides, polymers and carbon nanotubes (CNTs).

These materials have different mechanism to detect the hydrogen ions in the acidic and alkaline solution. They have some advantages and disadvantages which we mention in this chapter. Chemiresistive sensors are fabricated from the conductive electrodes and one of the best option is silver (Ag).

3.2 Metal oxides

Today, metal oxides (MOx) are used for diverse applications in nanostructures due to their physical and chemical properties, RuO_2, IrO_2, TiO_2, ZnO, RuO_2, MnO_2, etc are examples of metal oxides. Metal oxides are utilized in various sensors and ion-selective material, including gas, temperature, and pH. The most common sensors that utilize metal oxides in their fabrication process as an active material are pH sensors. MOx is used in different types of pH sensors such as ios selective field transistors, electrochemical pH sensors, and chemiresistive pH sensors. The pH level of a sample solution and the concentration of ions can alter the electrochemical properties such as impedance and potential of the electrodes. These kinds of pH sensors which are fabricated from MOx are used in different industries such as food industries, water pollution assessments, and biomedical applications. The sensitivity MOx pH sensors are related to the composite and deposition method which affect the surface homogeneity and the structure of the material. Some of MOx is used in chemiresistive pH sensors which work based on the changes in electrical resistance between the electrodes (Manjakkal *et al.*, 2020).

3.2.1 pH sensing Mechanism of metal oxides in chemiresistive pH sensors

Chemiresistive sensors do not require a reference electrode(RE). The sensitive material is deposited between the conductive material. A semi-conductive composite of metal oxides is deposited between the two conductive electrodes. By altering the H_3O^-/OH^- concentrations, the electrical properties such as conductivity and electrical resistances are changed. It causes by the protonation and deprotonation of the sensing material (MOx). In the acidic solutions conductivity increases and electrical resistances decreases. In the alkaline solutions it does the opposite. The schematic of a chemiresistive sensor based on metal oxides (MOx) is shown in figure 3.1 (Manjakkal *et al.*, 2020).

Metal oxides have some disadvantages which they are not suitable to be used in smart bandages for instance (Manjakkal *et al.*, 2020)e:

- They are very sensitive to the components of alkiline and acidic sample solutions.

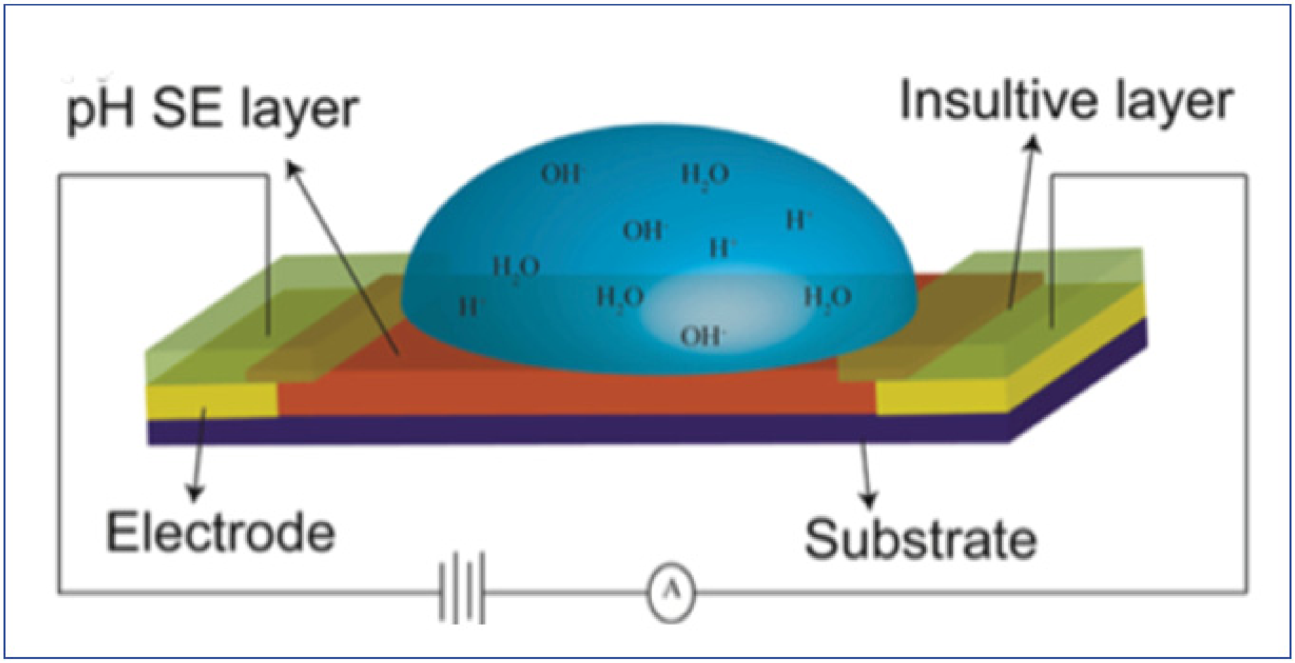

Figure 3.1 Metal oxides used as the pH sensitive material in a chemiresistive pH sensor Manjakkal *et al.* (2020).

- They are not suitable for blood monitoring and biomedical applications.
- They just detect the limited range of pH.
- They show slow accuracy and resolutions.

3.3 Carbon Nanotube (CNT)

Nanotubes are materials that are up to about 100 nanometers in diameter. The term nanotubes are generally used to refer to carbon nanotubes. Carbon nanotubes have a cylindrical structure that is, a hollow tube that walls are made of carbon atoms. Carbon nanotubes(CNTs) are one of the most important and widely used carbon structures recently discovered. They have unique properties and characteristics. Carbon nanotubes, in addition to being very strong, also have good flexibility and flexibility. One of their applications is composite. The most important property of nanotubes is their electrical conductivity, the value of which varies depending on the order of the atoms. They are cylindrical molecules with open or closed ends. The structure of the nanotubes is like a sheet of rolled graphite. Carbon nanotubes are hollow ring structures composed of carbon atoms that can be arranged in single or multi-walled form, and also have metallic and quasi-conductive properties. Carbon nanotubes have a very high specific surface area, high permeability, and good mechanical and thermal stability. Although the porosity of carbon nanotubes is significantly small, Nanotube membranes have been shown to have higher or uniform current intensities than much larger porosities due to the smooth inner surface of the nanotubes. These materials are durable and heat resistant (Chen *et al.*, 1998).

The most important physical property of nanotubes is their electrical conductivity. The electrical conductivity of nanotubes varies greatly from category to category, depending on the angle and type of bond; Each atom is vibrating in its place. When an electron (or electric charge) enters a set of atoms, the atoms vibrate more and transmit the applied electric charge when they collide with each other. The higher the order of the atoms, the greater the electrical conductivity of those nanotubes (Chen *et al.*, 1998).

There are two types of carbon nanotubes; Structurally, carbon nanotubes can be thought of as folded graphite sheets. Carbon nanotubes are classified in two different groups, SWCNT single-walled nanotubes and multi-walled MWCNT. They also are different in terms of physical properties as shown in 3.2 (Popov, 2004).

Multi wall carbon nanotubes (MWCNT); Multi-walled carbon nanotubes (MWCNTs) are also cylindrical with several concentric layers of graphene. They have a relatively complex structure and diversity.

single wall carbon nanotubes (SWCNT); Single-walled carbon nanotube (SWCNT) is a cylinder composed of only one layer of graphene. It shows unique electrical properties.

Single wall carbon nanotube is a better option than multi wall carbon nanotube to utilize in smart bandages regarding the reasons which are listed below (get.tuball) :

- SWCNTs have smaller diameter than MWCNTs, resulting in higher aspect ratio(length-to-diameter ratio) and more flexibility.

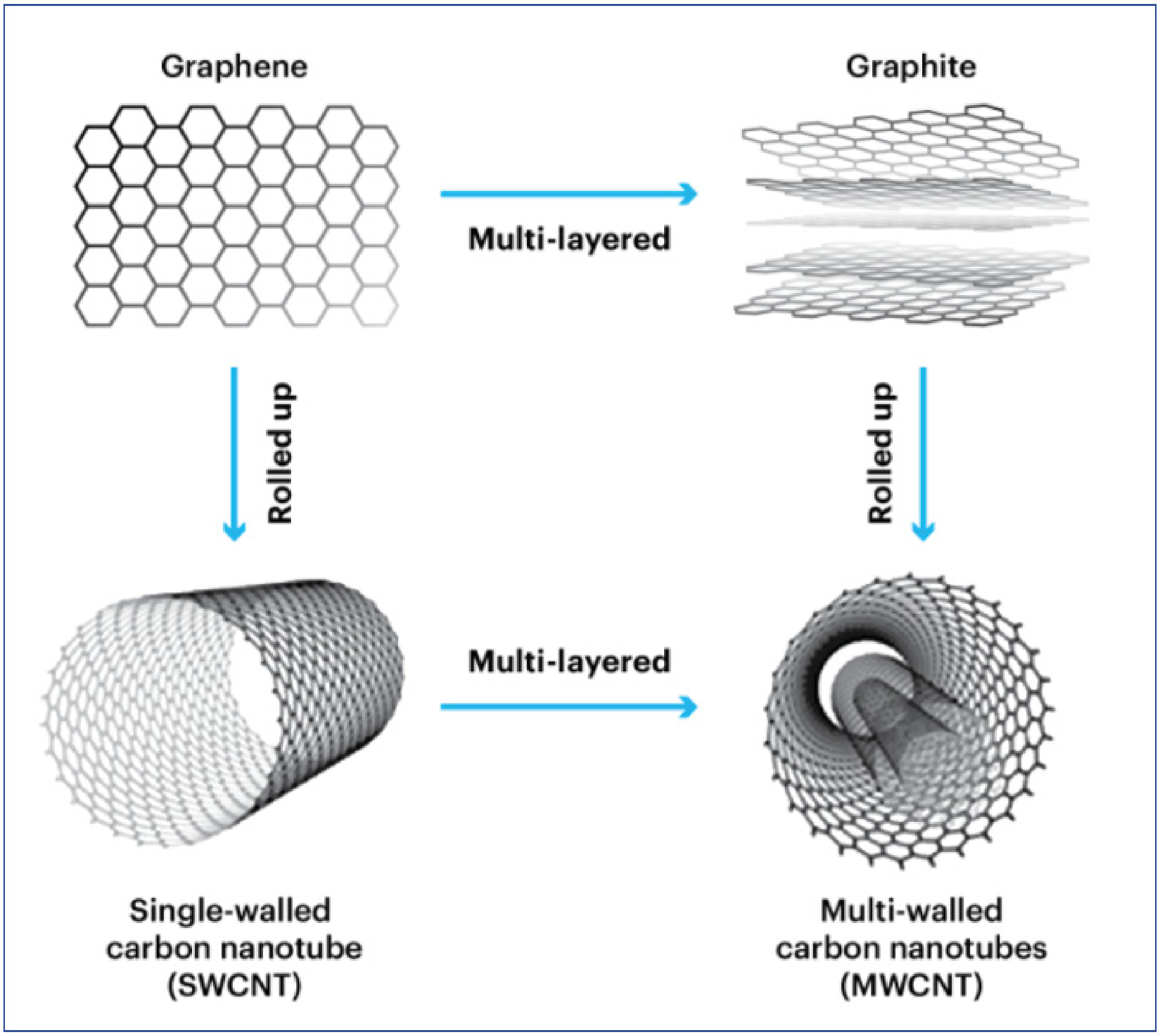

Figure 3.2 Single wall carbon nanotube and multi wall carbon nanotube structure get.tuball

- Unlike SWCNTs, MWCNTs can not be bent, folded and return to their original structures.
- SWCNTs have high tensile strength which make the different composite material strength, specially in polymer composites.
- SWCNTs are more cost effective than MWCNTs.

3.3.1 pH sensing Mechanism of Carbon Nanotube in chemiresistive pH sensors

Figure 3.3 exhibits the mechanism of hydrogen ion sensing by SWCNTs. C-O and C-H bonds on the surface of the SWCNT and also the concentration of H^{+} in the alkaline and acidic solutions plays vital role in the sensing mechanism (Jeon *et al.*, 2020a).

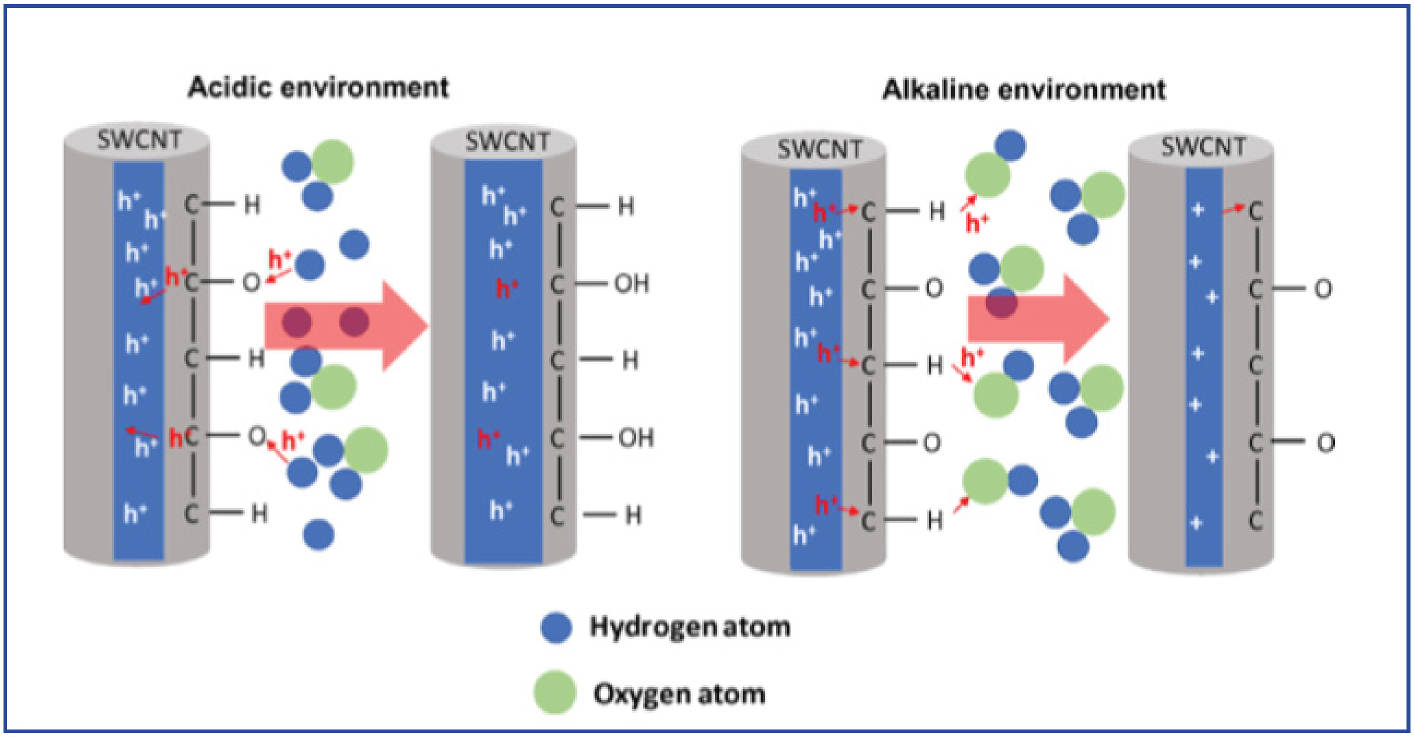

Figure 3.3 H^{+} Sensing mechanism of SWCNTs Jeon *et al.* (2020a)

When signle wall carbon nanotube is exposed to an acidic solution H^{+} is absorbed by the oxygen atom in C-O bonds in SWCNT, resulting in potential of the SWCNT's surface positively charged and decrease the resistance of the chemiresistive pH sensor and increase the conductivity.

By dipping SWCNT in the alkaline solution which included OH^{-}(negative radicals), H^{+} (positevly charged) is eliminated from C-H bond, resulting in increasing the resistance of the chemiresistive pH sensors and decreasing the conductance (Jeon *et al.*, 2020a).

3.4 Polyaniline (PANI)

The chemical and physical properties of polymers themselves have several properties, which is the main reason for the constant use of polymers in electronic measuring devices. In recent years, polymers have become very important as sensory elements in synthetic sensors. With the replacement of polymers by classical materials in sensors, high selectivity and accurate measurements have been achieved, in which nanotechnology and the main or secondary properties of polymers have been used. Polyaniline is one of the most important conductive polymers and belongs to the family of semi-flexible rod polymers, which was discovered in 1834 from the polymerization of aniline. In the structure of Polyaniline, the presence of reactive NH groups in the polymer chains maintained on both sides with phenylene groups has created special properties such as good electrocatalytic activity, high conductivity, easy preparation and environmental stability. In recent years, extensive studies have been performed on this polymer for use in electrochemical devices, rechargeable batteries, chemical and biological sensors, and solar cells (Kwon & McKee, 2000).

Polyaniline has different structures that have different physical and chemical properties, which are classified mainly into three groups (Kwon & McKee, 2000) as exhibited in figure 3.5 and figure 3.4:

- leucoemeraldine base (LB; fully reduced form)
- Emeraldine base (EB; half oxidized form)
- Pernigraniline base (PNB; fully oxidized form)
- PANI (ES) is the dopped form of PANI(LB) or PANI (EB).

The amount of electrical conductivity at the surface of the green protonated emeraldine salt(PANI (ES)) is greater than that of ordinary polymers and less than that of ordinary metals. An emeraldine base (EB; half oxidized form) is easily protonated by dopping in the acidic solution such as HCL. This leads to a significant increase in conductivity and the production of positive charges in the polymer network. This is while the number of electrons in the polymer structure remains constant. Thus, in the protonated state of emeraldine, called emerald salt, new optical, electrical, and para-magnetic properties are created. Soluble polyaniline for a variety of reasons, including conductivity Suitable electrical and high solubility in alkaline aqueous solutions is very important. Nowadays, the design of new materials based on polymer, including polymer nanocomposites, has very special properties Creates. These compounds have advantages such as lightness, special strength, high durability, and lower cost. Synthesis and application of polyaniline nanocomposites with other materials in organic solar cells and chemical sensors are one of the solutions offered to improve their properties in recent years (Bejbouji *et al.*, 2010)-(Kwon & McKee, 2000).

Nanocomposite components can be combined in different ways. In the synthesis of polyaniline-based nanocomposites, the composite is usually added during the polymerization of the polyanylene, and the rest of the steps are similar to the synthesis of this polymer. This synthesis is done by two methods of chemical oxidation and electrochemical oxidation. Conditions such as the amount of oxidant to monomer ratio, oxidant type, type of solvent and acid, temperature and pH of the solution have a significant effect on the properties of the prepared polymer nanocomposite such as conductivity and morphology (Stejskal & Gilbert, 2002). Chemical synthesis methods include the use of pattern molecules such as acitive materials on the surface, nucleation methods, fast mixing reactions, and slow mixing methods. Over the past few years, polyaniline carbon nanocomposites such as graphene-polyaniline have attracted much attention due to their new properties and very diverse applications. These nanocomposites show better properties compared to polymer and carbon material alone (Wang, Lu, Lei & Song, 2014).

3.4.1 pH sensing Mechanism of Polyaniline in chemiresistive pH sensors

By exposing conductive form of PANI as an active material in a acidic alkaline solution, nitrogen atoms in PANI structure absorb H^+, oxidation is happening and PANI is getting protonated. Resulting in, Conductivity increases and the resistance between the two electrodes of the chemiresitive pH sensor decreases.

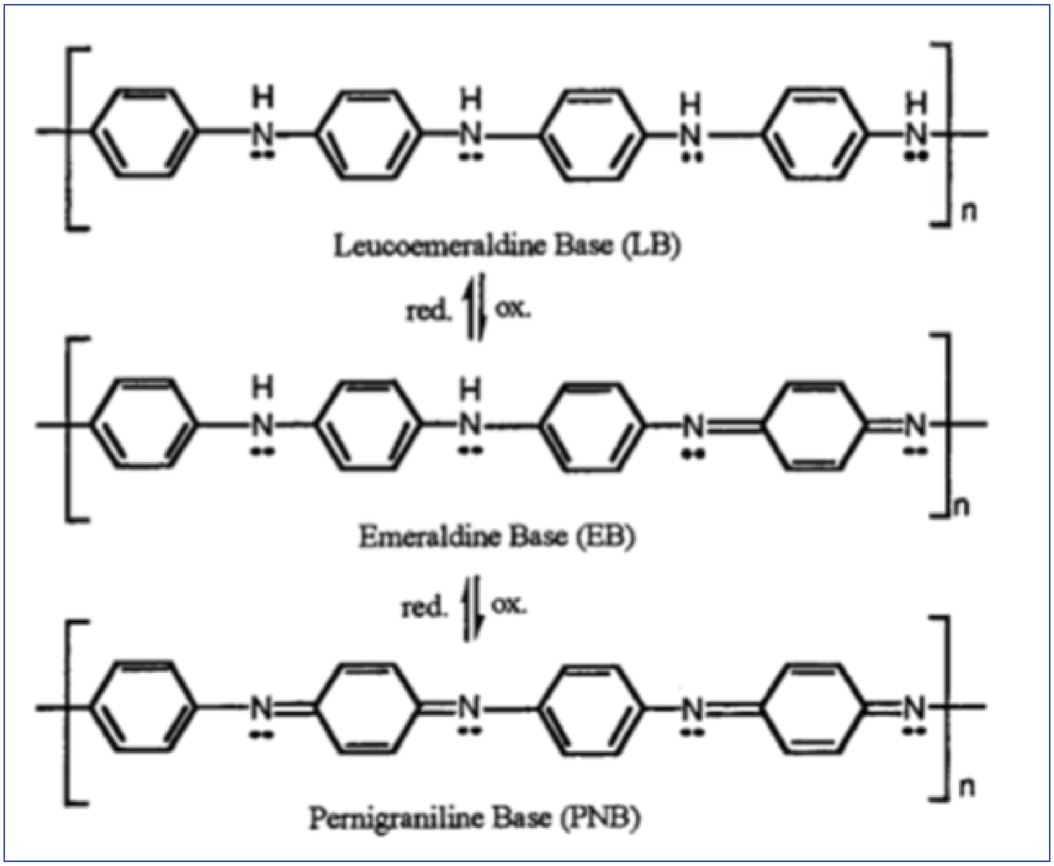

Figure 3.4 Classification of PANI structures Kwon & McKee (2000).

In the alkaline solution, PANI does the opposite. H^+ ions are withdrawn from the nitrogen atom in PANI and its getting deprotonated. The conductivity between the chemiresistive sensor's electrodes decreases and the resistance increases (Chinnathambi & Euverink, 2018)-(Jeon *et al.*, 2020b).

3.5 Polyaniline/carbon nantube composites

Due to the unique electrical, thermal, mechanical, optical and electrochemical properties of carbon nanostructures, these materials are used as a material to combine with various types of materials such as metal nanoparticles, polymers and organic metal compounds. One of the most common carbon nanocomposites is polymer nanocomposites. These nanocomposites show

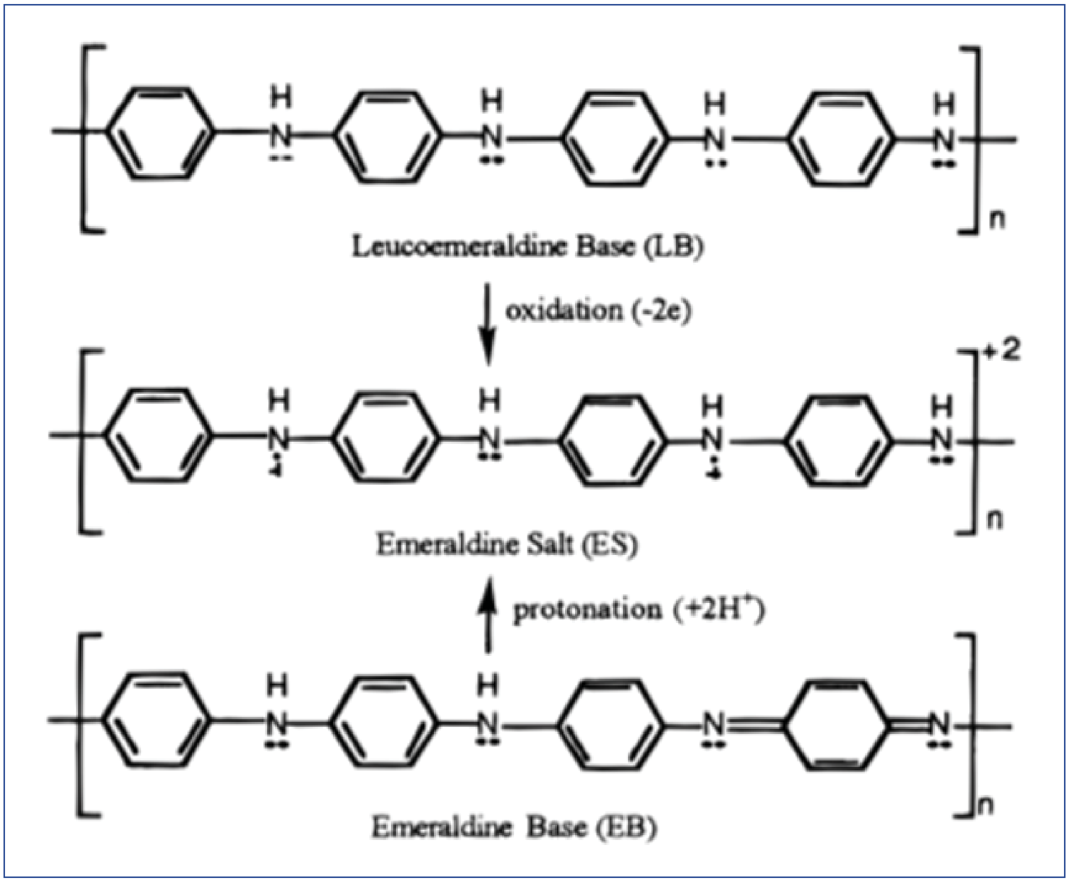

Figure 3.5 Different types of PANI structures Kwon & McKee (2000).

better properties compared to polymer and carbon material alone (Jeong, Kim, Han & Park, 2015)-(Wang *et al.*, 2014).

In recent years, polyaniline nanocomposites - carbon nanotubes have been one of the most widely used carbon-based compounds in chemical sensors. Since the discovery of carbon nanotubes (CNTs), a wide range of carbon nanostructures such as single-walled (SWNT), double-walled (DWNT) and multi-walled (MWNT), graphite nanofibers, carbon nanofibers and carbon nanofibers have been discovered. The atomic and electronic structure of carbon nanotubes creates unique thermal, electrical, and mechanical properties such as low weight and high hardness, which have attracted the attention of many scientists today. The combination of polyaniline and carbon nanotubes leads to the formation of composites with much better properties than pure components (Wang *et al.*, 2014). The structure of PANI/CNT composite is presented in 3.6.

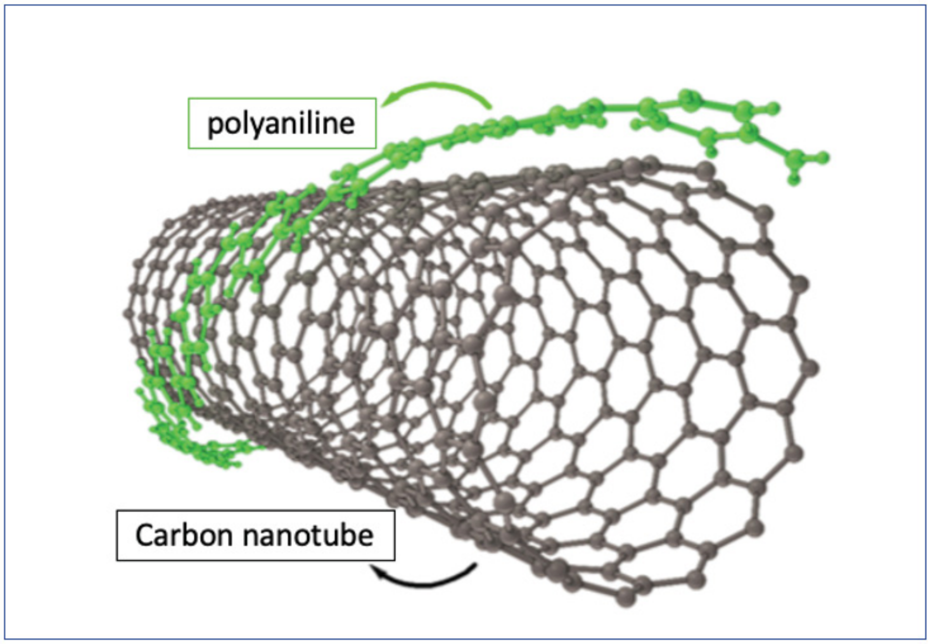

Figure 3.6 PANI/CNT composite Salvatierra *et al.* (2015).

3.6 Hydrogen sensitive materials in our chemiresistive pH sensor

Single-walled carbon nanotube (SWCNTs) are pH sensitive by a protonating/deprotonation process SWCNTs . The SWCNTs surface becomes positively charged through an increase in conductivity. Contrarily, protonation oxygen atoms in the acidic medium, leading to he surface becomes negatively charged through the deprotonation of carbon atoms leading to a decrease in conductivity. However, SWCNTs can only detect a narrow pH range, lacking sensitivity in higher pH value environments. When the value of the pH is in the alkaline medium, higher than the carbon isoelectric point, the surface of the CNT becomes negatively charged and electrostatically limits its interaction with cations (Emami *et al.*, 2021)

Differently, polyaniline is an efficient pH sensing material, especially in higher pH values. The chemiresistive pH sensor-based PANI (ES) function depends on the protonation/deprotonation process of the amine groups at different pH levels .

The suggested sensor is used without the need of a reference electrode. The chemiresistive pH sensor works on the basis of measuring the resistance of the active layer between two silver (Ag)-electrodes in the presence of a target solution. SWCNTs were used in this study for their outstanding chemical, mechanical and electrical characteristics in fabricating conductive networks. PANI was used because its electrical conductivity can change depending on its oxidation state at different pH solutions. Furthermore, it is easy to manufacture (Emami *et al.*, 2021). Here, we prepared ex-situ SWCNT/PANI (ES) nanocomposites, unlike in situ composites, which do not require aniline polymerization. Using ex-situ composites makes the manufacturing process more straightforward. The pH's sensitivity and signal stability were improved upon drop-casting an additional PANI (ES) layer on top of the SWCNT/PANI (ES) nanocomposite layer.

3.7 Material

The materials which were used in our research project based on literature are listed below:

- P2-SWCNT powder obtained from Carbon Solution
- Sodium dodecyl sulfate (SDS) powder from Sigma-Aldrich
- PANI (ES) powder from Sigma-Aldrich.
- PANI (EB) powder from Sigma-Aldrich.
- N- methyl-2-pyrrolidone (NMP) were purchased from Sigma- Aldrich.
- Silver ink for screen printing was obtained from DuPont.
- Standard pH solutions were obtained from Cole Parmer.
- Carbon black paste for screen printing was acquired from Henkel.
- lime juice was used as the pH 2 solution.
- The pH values of the solutions were verified by a pH meter (Accumet AB 15/ 15+ bench-top meter).

Figure 3.7 P2-SWCNT powder

CNT and PANI were used as the hydrogen sensetive materials. SDS powder were used to make a uniform CNT solution. NMP is proper solvent for PANI.

These materials are generally in powder form and must be dispersed in a suitable solvent in order to form a film on a flexible substrate.

3.8 Preparation of aqueous SWCNTs dispersion

SWCNTs dispersion was prepared by mixing 0.1 g of P2-SWCNT for 15 minutes with 0.25 g of SDS pre-dissolved in 100 mL of DI water.

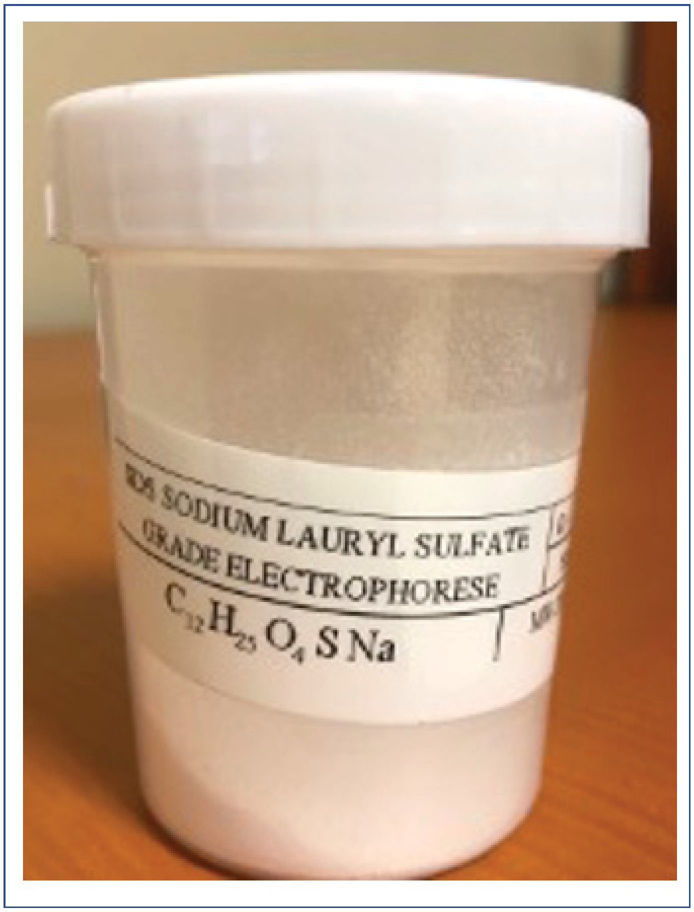

Figure 3.8 Sodium dodecyl sulfate (SDS) powder

Next, the mixture was placed in a sonication bath (VWR® Ultrasonic Cleaners, 220V) for 5 hours at 21 °C.

The dispersion was subsequently centrifuged at 3500 RPM for 20 minutes to remove the unexfoliated nanotubes from the supernatant.

3.9 Preparation of aqueous PANIs dispersion

the PANI dispersion was achieved by sonicating 10 mg of PANI in 1 ml NMP solvent for 15 minutes at 21 °C.

CNTs are one of the most well-known materials in the field of pH detection, but they do not perform well at high pH levels. Therefore, in the structure of these sensors, we used PANI as a hydrogen-sensitive material that performs well in both acidic and basic environments. These materials are generally in powder form and must be dispersed in a suitable solvent in order to form a film on a flexible substrate. The size of this sensor is small and it is designed for smart bandage. According to the application that may have in the future, this size can be changed.

3.10 Conclusion

Based on the literature which we reviewed, three common groups of hydrogen-sensitive material are used in different types of pH sensors, such as potentiometric pH sensors, ion-selective field transistors, and chemiresistive pH sensors. Metal oxides are used in chemiresistive pH sensors based on their physical and electrical properties although they have some disadvantages such as limited range of pH detection, low accuracy and they are not suitable for biomedical applications such as blood monitoring. Carbon nanotubes are one the most common hydrogen-sensitive material in pH detection. CNT is classified into two different groups; multi-wall carbon nanotube and single wall carbon nanotube. Due to their higher flexibility, aspect ratio and tensile strength SWCNT is more suitable than MWCNT to be used in chemiresistive pH sensor which is used in smart bandages. Some types of polymers are hydrogen sensitive. The most important of them based on the unique chemical and physical properties is polyaniline.

In conclusion, the combination of polyaniline and carbon nanotube improves the formation of nanocomposites with much better properties than pure components.

CHAPTER 4

CHEMIRESISTIVE PH SENSOR FABRICATION METHODS AND PROCESS

4.1 Introduction

There are several ways to fabricate electronics. The most important point in choosing the right method is the materials that are used in the fabrication process. In addition, cost-effectiveness must be taken into account. The quality of the deposited composite on the substrate is related to the properties of the material components, deposition techniques, and also the properties of the desired substrate. The desired film must be homogeneous and uniform on the substrate and shows good sensitivity.

In this chapter, the most important deposition techniques such as lithography, inkjet printing, drop-casting, liftoff, and screen printing method will be reviewed.

4.2 Lithography

Lithography is an engraving in nanoscale. This manufacturing method is a top-down method that is widely used in the electronics industry. Using lithography, specific geometric patterns are created on a substrate. To create these patterns, you can use light, electron beams, stamping techniques in nano-dimensions, etc., and create the desired design with or without a mask. Lithography is widely used to produce transistors, integrated circuits, and electronic components (Thompson, 1983).

Lithography is generally the operation of transferring geometric patterns to a substrate. Lithography is widely used to produce transistors, integrated circuits, and electronic components. Lithographic methods are divided into two categories; Lithography using a mask and lithography without a mask. In mask lithography, a mold or mask is used to transfer the patterns on a large scale and can produce tens of wafers per hour. Types of lithography with masks include optical lithography, soft lithography, and lithography with nano-dimension sealing. On the other hand, maskless lithography such as electron beam lithography, concentrated ion beam lithography and scanning probe lithography produce the desired patterns without the use of a mask. These methods create serial patterns that allow us to create custom designs in nano-dimensions. However, the operational capacity of this type is limited because its sequence is slow and unsuitable for mass production (Robinson & Lawson, 2016).

4.2.1 Optical lithography(photolithography)

Optical lithography is the main production method in the semiconductor and integrated circuit industries. This method is used in modeling to build integrated circuits, microchips, and electromechanical microsystems(MEMS). In this method, a light-sensitive polymeric material (photoresist) is exposed to ultraviolet light and the desired patterns are created. Initially, ultraviolet light with a wavelength range of 193-436 nm is emitted through a photo mask. The photo-mask consists of a transparent surface such as glass or quartz on which matte patterns are layered. At the surface of the photoresist that is exposed to radiation, the polymer chains break down and its solubility in a chemical solution called the enhancer increases. The substrate is then immersed in the curing agent and the exposed part is removed. Figure 4.1shows the schematic view of optical lithography (Li & Wang, 2012).

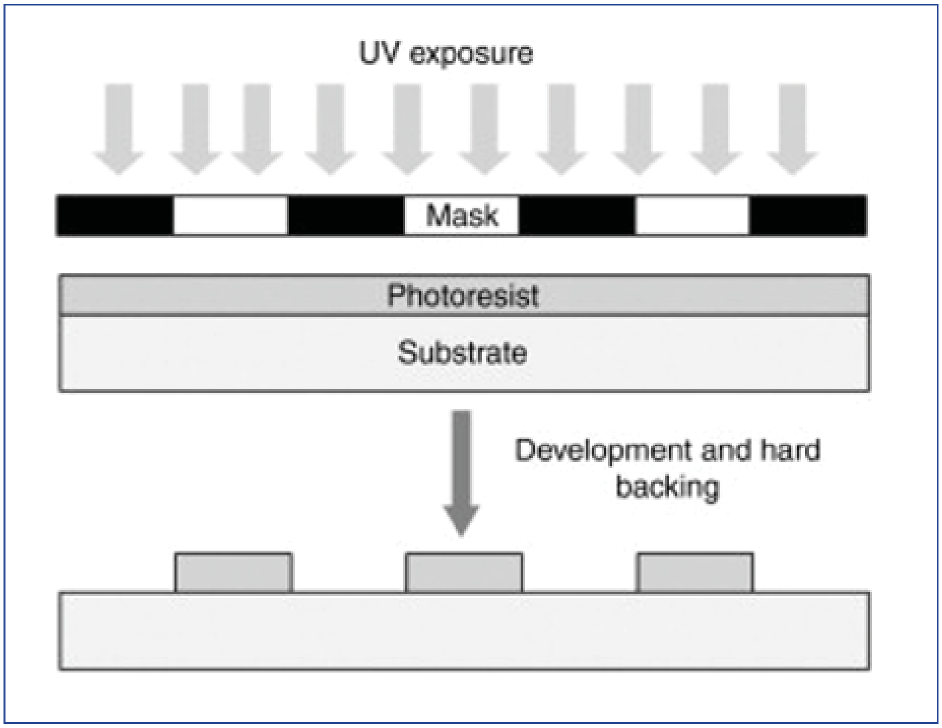

Figure 4.1   Optical lithography steps Li & Wang (2012)

4.3 Aerosoljet printing

Aerosol jet printing, as a direct and non-contact technique, is commonly used for printing circuits and conductive components on different types of substrates. Aerosoljet printing uses aerodynamic concepts to deposit colloidal suspensions on the substrate. It also makes it possible to deposit without a mask or contact. In addition, due to the large distance between the nozzle and the substrate, aerosol jet printing can also be used for Complex patterns, and structures can also be printed on textured, stepped, or curved surfaces (Huang & Zhu, 2019).

4.3.1 Aerosol jet printing of nanomaterials

Silver electrodes were layered on printed circuit boards using silver nano-particle ink and aerosol jet printing. Due to the relatively high height of the printer nozzle from the substrate and the long focal length of the material flowing out of the nozzle, aerosol jet printing is an ideal solution for printing on non-flat surfaces. Stratification of conductive components at room temperature was achieved with the help of plasma patterns and silver nano-wires. These patterns create a highly interconnected network that covers deep and superficial gaps between the plastic fibers of the non-three-dimensional substrates. In addition to printing on non-three-dimensional substrates, aerosol jet printing can also be used to build three-dimensional structures (Huang & Zhu, 2019).

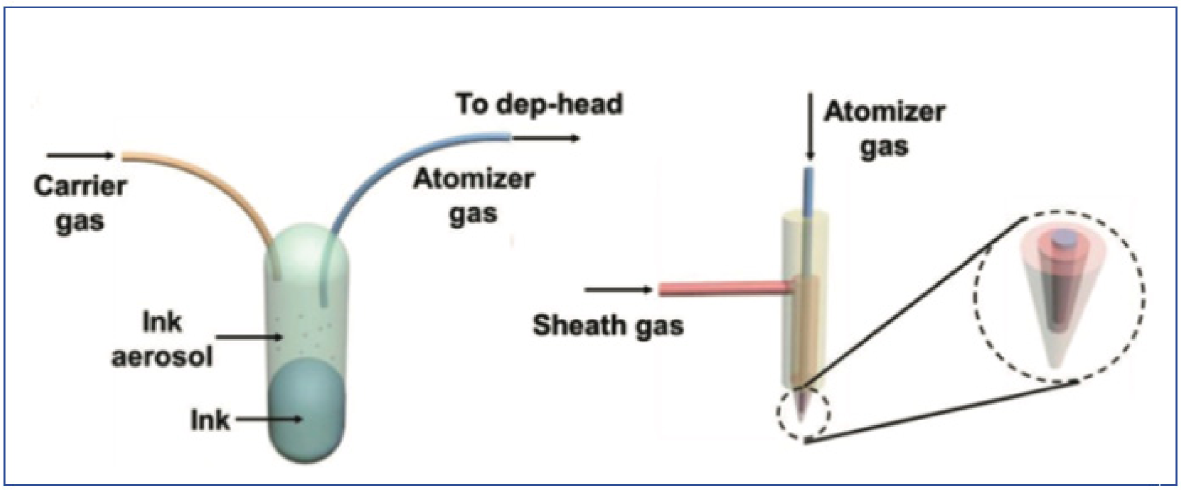

Figure 4.2 Schematic of aerosol jet printing Huang & Zhu (2019)

Aerosol jet is a complex method and requires nano-materials with high viscosity. Figure 4.2 shows a schematic view of Aerosol jet printing.

4.4 Drop-casting

As it is shown in figure 4.3, drop-casting is a simple, inexpensive, and easy method to fabricate a film on the desired substrate. The modified layer can be made by the components of nanomaterials such as carbon nanotubes. This method is commonly used in electrocatalytic analysis and electrochemical sensing techniques. Nano-Materials should be mixed in a proper solvent via ultrasonication and caste by dropping on a targeted flat substrate and followed by curing in the oven (Kanoun *et al.*, 2014) -(Bormashenko *et al.*, 2019).

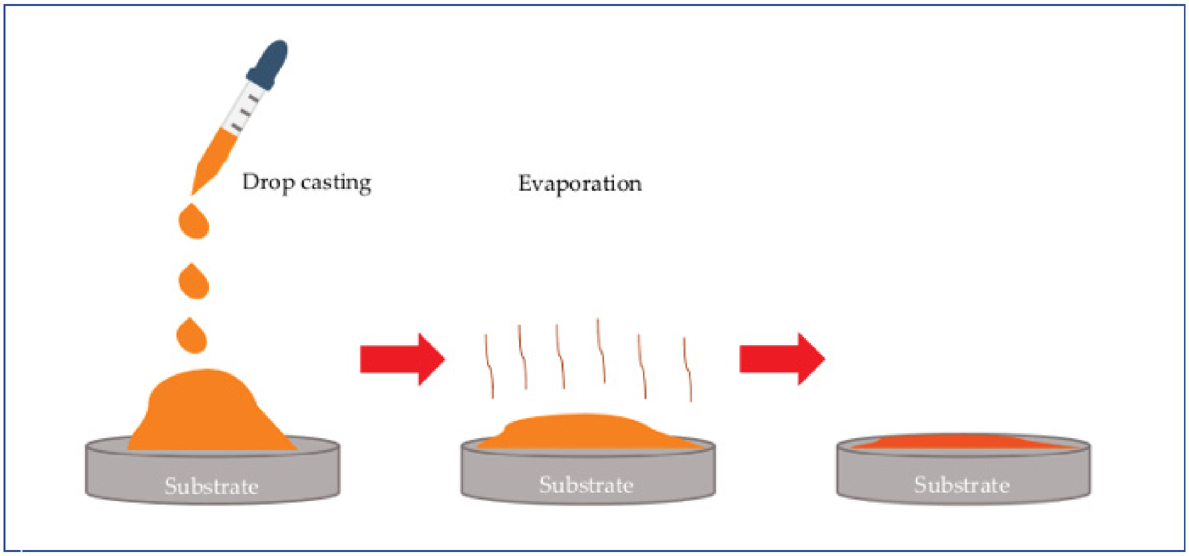

Figure 4.3 Schematic of drop-casting Bormashenko *et al.* (2019)

4.5 Screen printing

Recent studies have shown that the electronic printing method is now Becoming a method for making electronic components with high surface area and flexibility, by creating patterns by inks made of functional materials. Flexible electronic components and the Internet of Things (IoT) as an innovative technology are gaining a lot of attention that will drastically change our lives. Innovation in screen-printing technology has made it possible to make bulky electronic components at low cost and on soft materials such as plastic, paper or fabric. This will make the printed parts more flexible (Picallo *et al.*, 2019)-(Wu, 2017).

Screen printing is an extraordinary technology that is used especially for printing inks on hard or flexible covers, and the whole method is very simple, versatile and inexpensive. In fact, screen printing is a fast method in which inks pass through the mask and settle on the substrate during the printing process. The mesh is often made of porous nylon fabric and the entire plate is stretched into an aluminum or wooden frame (Tomchenko, 2006).

4.5.1 Screen printing process

As it presented in figure 4.4, printable inks can penetrate areas of the designed pattern because these areas are open and other areas are blocked by light-sensitive materials to form a stencil. The mask plate is at the top and the inks are on the plate until all the mesh openings are filled. The operator then uses a squeegee to move the mesh to a substrate and presses it on the back of the screen. In mesh openings, the inks are pumped by the capillary effect or compressed to a controlled amount on the substrate. As the paint moves forward, the tension on the back of the screen decreases, removing the mesh from below and leaving the ink on the surface of the screen. Then we can get the patterns designed on the bed that can be used in the next step. In the printing process, the inks go through four stages: filling, contact, adhesion, and release. Printing of both inorganic and organic layers is possible using screen printing (Tomchenko, 2006) (Wu, 2017).

As our objective is to fabricate a pH sensor which is needed to be small, flexible, cost effective with specific design of conductive electrodes to be used in the smart bandage system and screen printing is the best technique to fabricate our chemiresistive pH sensor.

The screen printer machine which we used in our project was P200S from KEKO company exhibited in figure 4.5. An important point about this machine is that it can print multiple electrodes at the same time. This allows to have a large number of electrodes to fabricate the pH sensor in a short time. This machine accepts only a 10CMx10CM substrate size. It imprints via fills and conductive inks such as gold, silver and carbon black on desired substrate. It utilizes a metal mask with our desired electrode design to print the conductive paste. A metal grill-work with photosensitive emulsion is used to trace conductor lines.

To hold and fix the substrate for printing, it is necessary to drill holes in the four corner of the substrate. We have to use punch machine(PAM4s) from KEKO shown in figure 4.6. It is an optical system ensures perforating point accuracy.

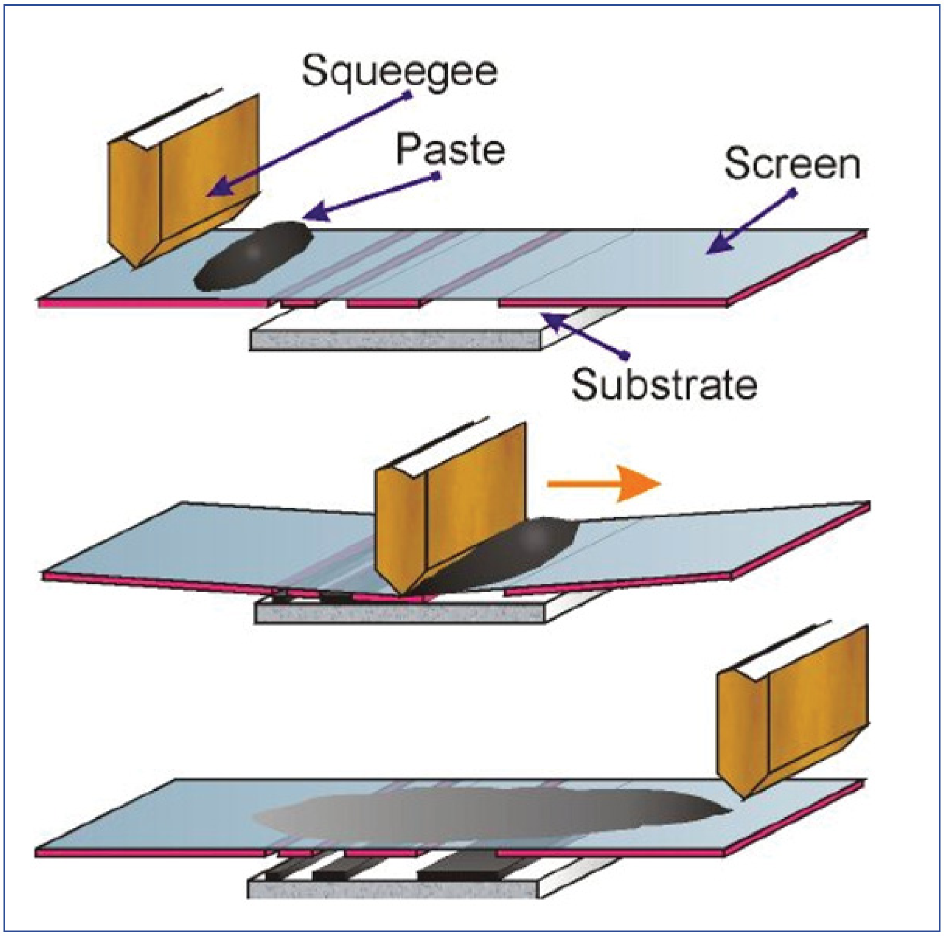

Figure 4.4 The basic screen-printing process Tomchenko (2006)

4.6 Design

Figure 4.7 shows the schematic design and dimensions of the Ag-electrodes with 30 mm length, 1 mm width, 5 m thickness and 100 m gap.

The size of the sensors can be changed throughout the design to embed specific wound sizes and geometries.

4.7 Fabrication process

1-In the first step, we designed the electrodes by AutoCAD as exhibited in figure 4.8.

Figure 4.5 P200S screen-printing machine

2-In the second step, a mask shown in figure 4.9 was prepared from the electrode's design for the screen-printing process.

3-Since the screen printer machine accepts only 10Cm x 10Cm substrate, PET was cut to 10by10 squares.

4-For fixing the substrate on the screen printer machine, 4 corners of substrate needs to be punched by punching machine.

5-In the second step the polyethylene terephthalate substrate was cleaned.

6- Silver paste provided by stirring it by hand and silver electrodes screen-printed on the pre-cleaned substrate by P200S, KEKO printer machine.

7- Ag electrodes have to be cured in the oven at at 120 °C for 2 hours.

Figure 4.6   PAM4s punching machine

8- Drop-casting a certain amount of aqueous SWCNT/SDS solution and PANI solution in NMP solvent on the Ag electrodes as the hydrogen sensitive material.

9- In the final step the sensor have to be cured in the certain temperature and time in the oven.

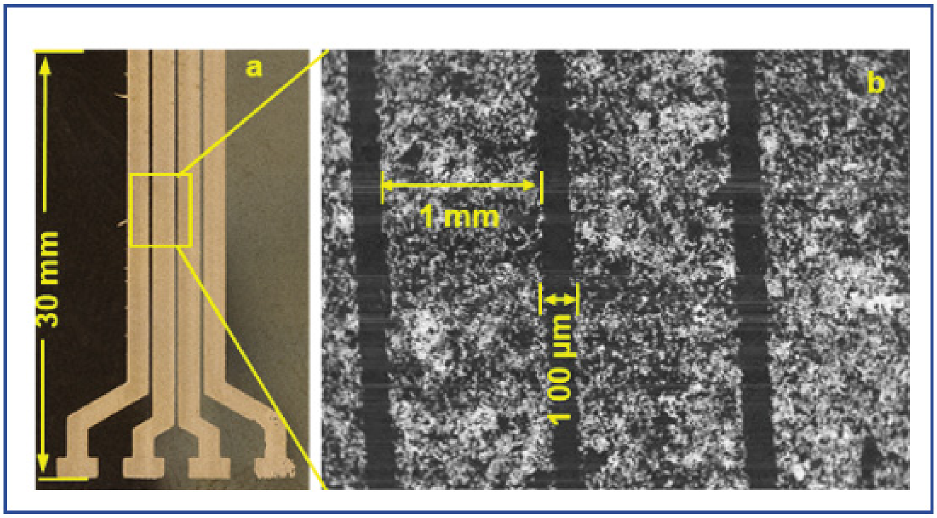

Figure 4.7 Schematic of chemiresistive pH sensor design

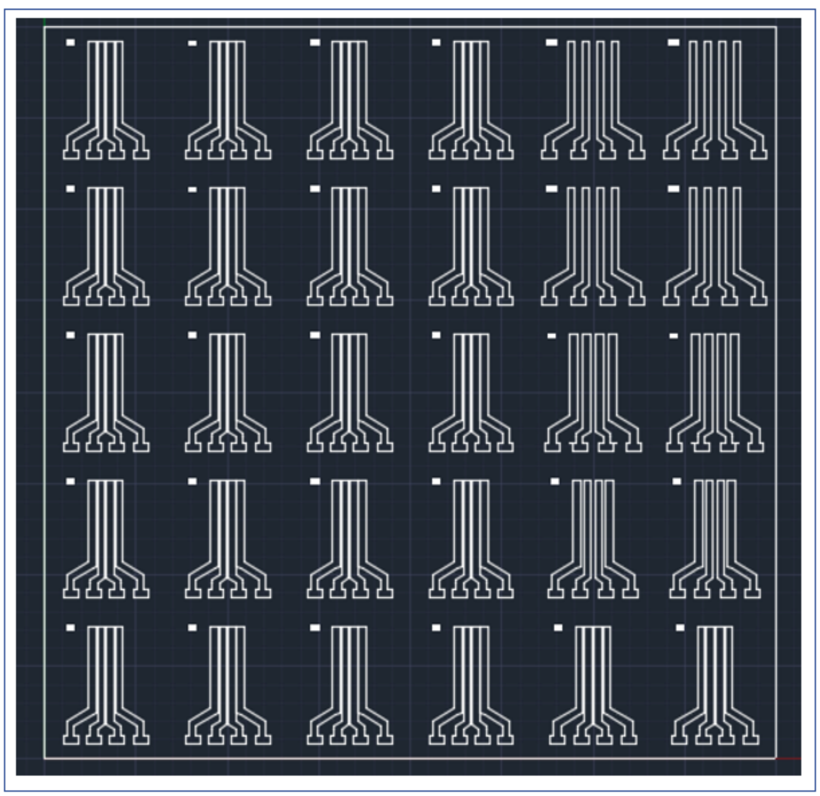

Figure 4.8 Electrode designed by AutoCAD

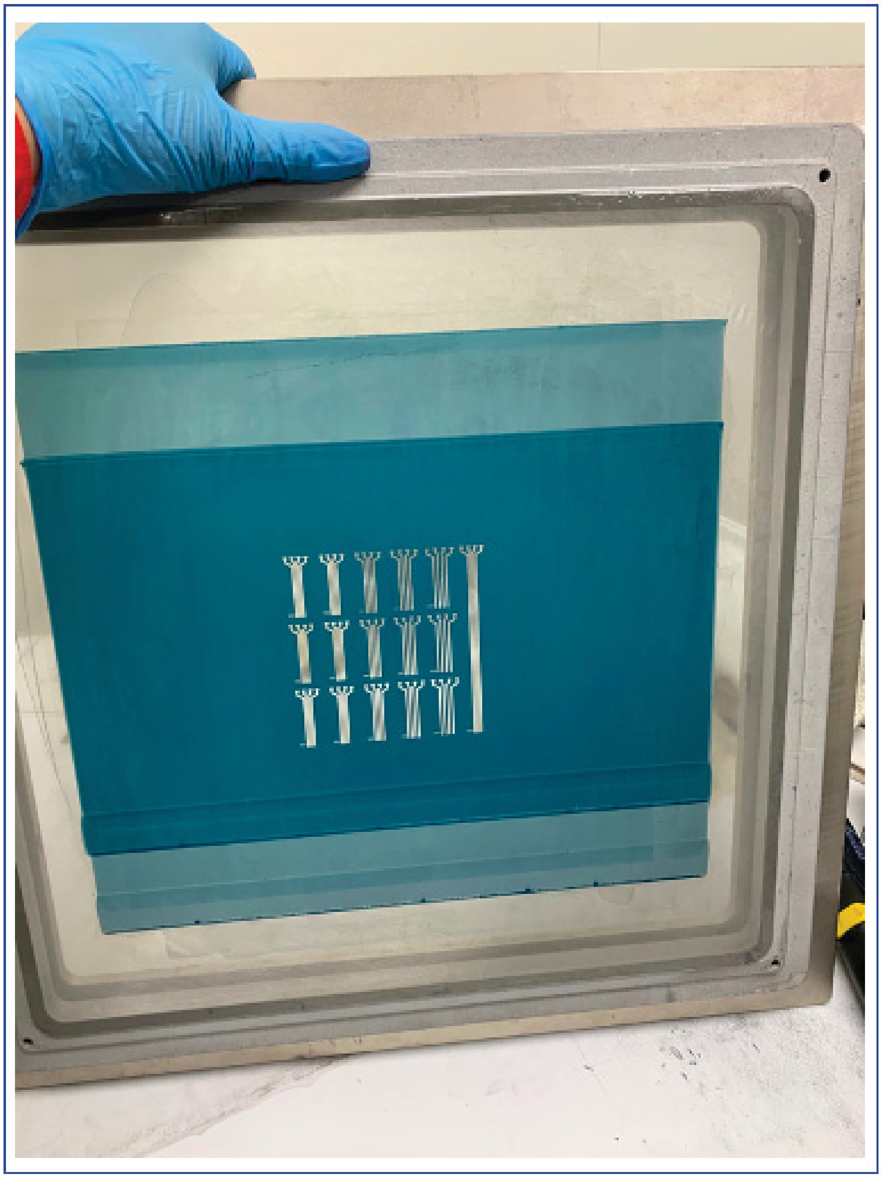

Figure 4.9 screen printing mask

4.8 Conclusion

In this chapter, common methods for making the electrodes needed to make sensors were reviewed. The first method was lithography, in addition to being a complex method, it is also generally suitable for printing electrodes on brittle glass surfaces. Aerosol Jet is a very complex method and requires a composite that has a high viscosity. Since composites consisting of CNT

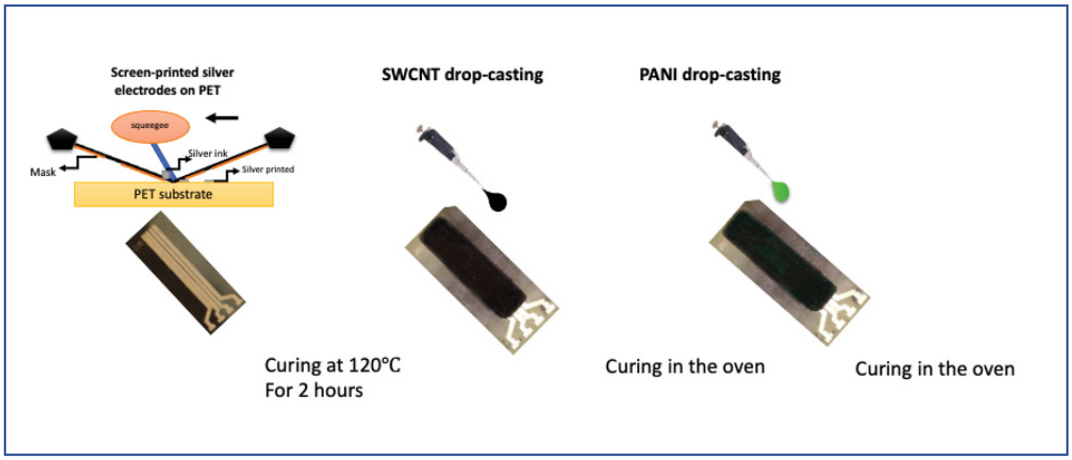

Figure 4.10 schematic of fabrication process of chemiresistive pH sensor

and PANI are often liquid, the aerosol jet is not a suitable method for printing these types of composites on desired substrates. Drop casting is a simple and easy way to form a layer of liquid composites on flexible substrates. This method can be combined with other methods. Screen printing is a reliable and repeatable method that can make small electrodes in large numbers and in a short time. It is easy to work with and does not have a complicated process.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Introduction

We tried different approaches to achieve the desired result as well as what we expected from a pH sensor. To fabricate a sensor that sensor has flexibility and does not react to different components during dipping the sensor in acidic or basic sample solutions. In each of these approaches we changed the parameters to achieve the desired method during the fabrication process. The most important optimizations that have been done in these approaches are the curing temperature of the sensor, the percentage of composite ingredients, using the best type of polyaniline group and also the method of forming a film on the flexible substrate. Since our research has been done on the fabrication of a chemiresistive sensor, measuring the electrical resistance between electrodes according to the behavior we expect from hydrogen-sensitive materials such as PANIs and CNTs can determine our results.

In this chapter, we will go into the details of the approaches performed as well as the results obtained from them.

5.2 Drop-casting PANI (EB) and SWCNT layer by layer

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 2.75 μL of aqueous SWCNT/SDS solution drop-casted on the silver electrodes.
- The sensor cured for 20 minutes at 120 °C.
- 2.75 μL of PANI (EB) solution in NMP solvent drop-casted on the SWCNT layer.
- Finally the sensor was cured at 120 °C for 2 hours.

The weight percentages (wt%) of the hydrogen sensitive materials(SWCNT and PANI (EB)) was the same and each was used in equal proportions.

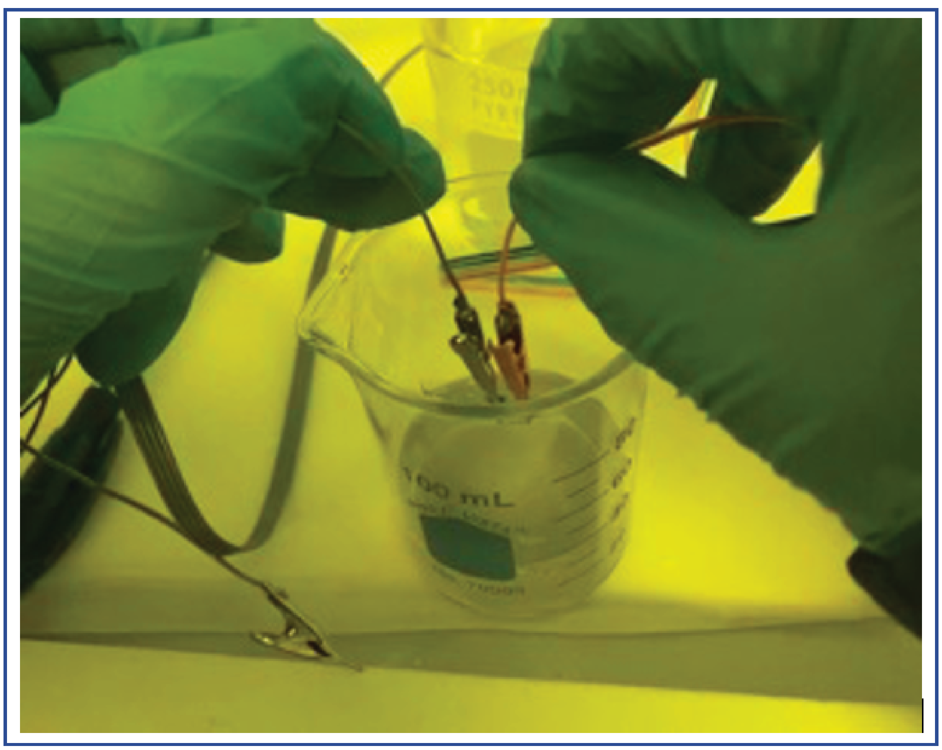

Figure 5.1 Dipping the sensor in a sample solution

5.2.1 Result and discussion

For pH sensing test, seen in figure 5.1 10 mA of constant current was applied between every two Ag-electrodes while the sensors were immersed in solutions with a pH ranging from 2 to 10. Simultaneously, a Keithley 2400 Graphical Series SMU measured the electrical resistance variation. The result for the first approach is presented in figure 5.2; In the first approach after dipping the sensor in acidic and basic solutions the constant current between the electrodes did not change, which means that the sensor could not detect the hydrogen ion, as a result the resistance of the sensor did not change. Based on this result the sensor could not detect the changes between the different pH levels.

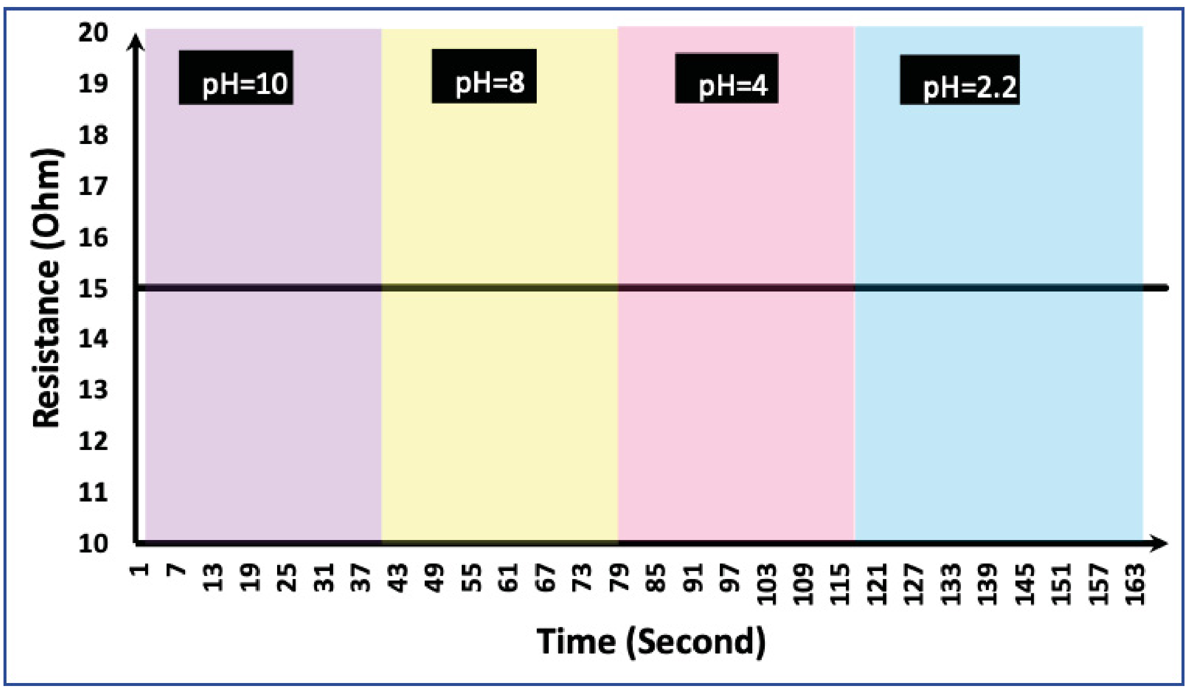

Figure 5.2 Electrical resistance changes after dipping the sensor in the pH 10,8,4,2.2

5.3 Drop-casting SWCNT/PANI (EB) composite

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.

- 5.2 μl of composite solution consisting of 50 (wt%) of aqueous SWCNT/SDS solution and 50 (wt%) of PANI (EB) solution in NMP solvent drop-casted on the silver electrodes.
- Finally the sensor cured for 2 hours at 120 °C.

Opposite of the first approach, in this approach, we used a PANI (EB)/SWCNT composite.

5.3.1 Result and discussion

For pH sensing tests, 10mA of constant current was applied by Keithley SMU between the electrodes and the sensor was immersed in the acidic and basic sample solution like the first approach. Then the electrical resistance was measured, shown in figure 5.3. As it is obvious in the result of the second approach, PANI (EB) can not detect and monitor the pH level in higher pH levels in basic solutions. PANI (EB) is the semi-conductive form of PANI, it has not enough and available Hydrogen ions to loose in basic solutions. As a result, it can not change the resistances between the silver electrodes in the basic sample solutions. On the other hand, PANI (ES) is a oxidized and conductive form of a PANI (EB). Not only it has available site to absorb hydrogen ions in acidic solutions but also has available hydrogen ions to loose in basic solutions.

5.4 Drop-casting SWCNT/PANI (ES) composite

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 5.2 μL of composite solution consisting of 50 (wt%) of aqueous SWCNT/SDS solution and 50 (wt%) of PANI (ES) solution in NMP solvent drop-casted on the silver electrodes.
- finally the sensor cured for 2 hours at 120 °C.

In this approach according to the above explanations we used PANI (ES) instead of PANI (EB).

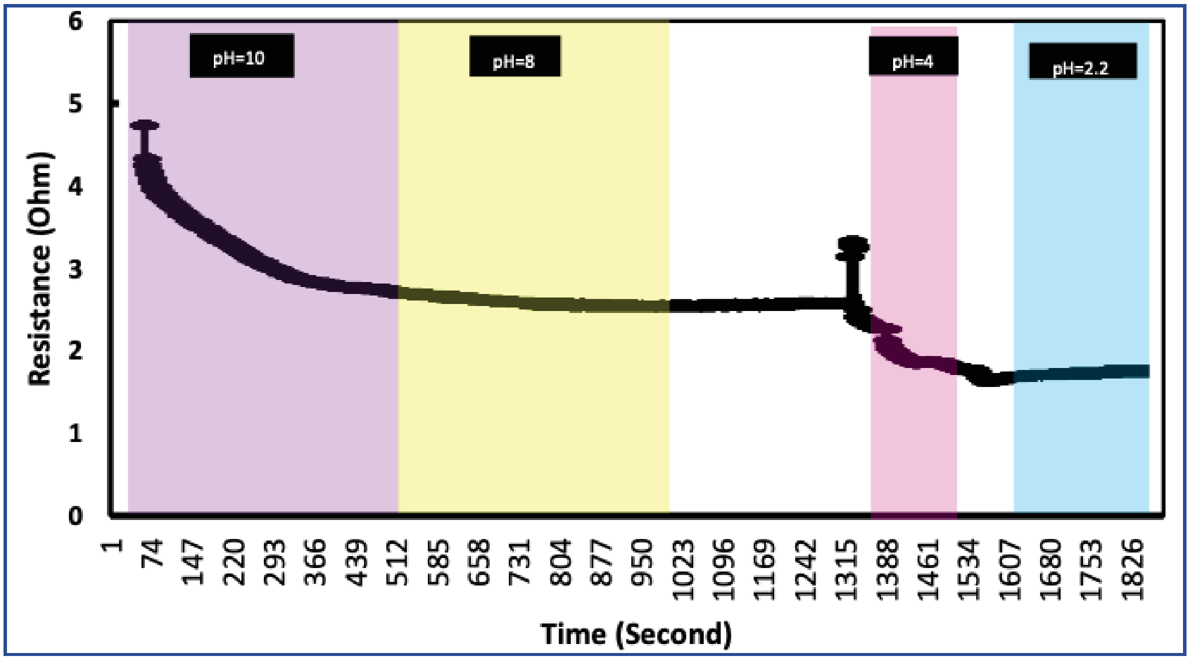

Figure 5.3 Electrical resistance changes after dipping the sensor in the pH 10,8,4,2.2

5.4.1 Result and discussion

The result of this approach is exhibited in 5.4. After removing the sensor from the oven, the composite film formed on the silver electrodes was very dry and broken. Some of the Ag electrodes which was screen-printed on the substrate were removed from the PET substrate shown in figure 5.4. We can mention the two important parameter which can have effect on the film breakage.The first one is curing time, and the second on is the temperature of the oven. To avoid the film breakage in the next approaches we optimized these two parameters.

5.5 Optimizing the temperature and time for sensor curing

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 5.2 μl of composite solution consisting of 50 (wt%) of aqueous SWCNT/SDS solution and 50 (wt%) of PANI (ES) solution in NMP solvent drop-casted on the silver electrodes.

Figure 5.4 Broken composite film and silver electrodes on the substrate

- finally the sensor cured for 2 hours at 90 °C.

In this approach we just focused on the optimization of the temperature for final curing the sensor to avoid film broken on the substrate.

5.5.1 Result and discussion

The result of this approach is exhibited in figure5.5. In this approach we reduce the curing time and the temperature of the oven. Composite film on the PET substrate was broken again. With the difference that the rate of film breakage at this temperature and the time, was less than the previous approach.

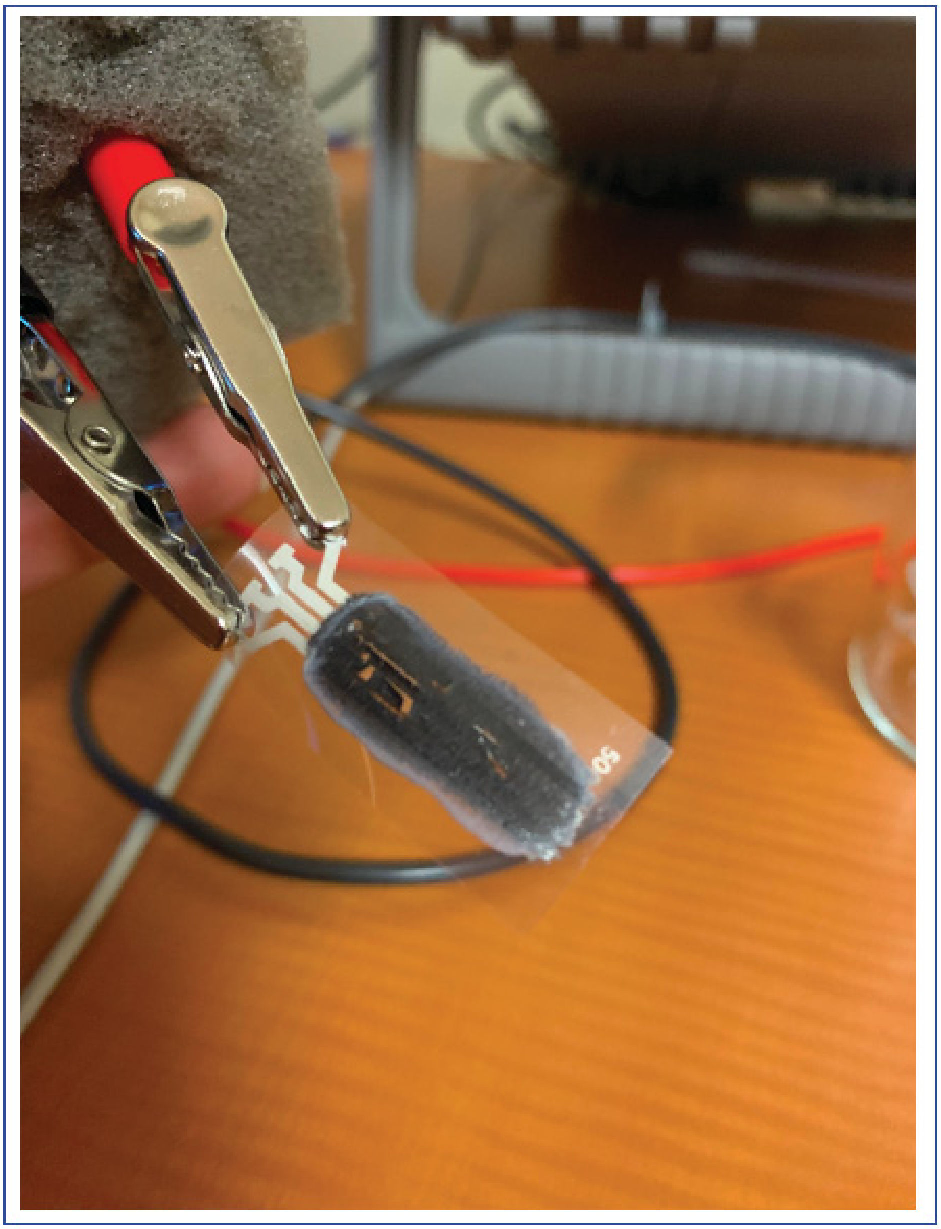

Figure 5.5 Broken composite film and silver electrodes on the substrate

5.6 Decreasing the oven temperature for sensor curing

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 5.2 μL of composite solution consisting of 50 (wt%) of aqueous SWCNT/SDS solution and 50 (wt%) of PANI (ES) solution in NMP solvent drop-casted on the silver electrodes.
- finally the sensor cured for 1 hours at 90 °C.

In this approach, the sensor was cured only for 1 hour.

5.6.1 Result and discussion

For the pH sensing test, 10mA of constant current was applied by Keithley SMU between the electrodes and the sensor dipped in the different sample solutions with different pH levels. As the result we can see that the electrical resistance changed in the different acidic and basic sample solutions shown in figure 5.6. After trying different temperature and time, curing at at 120 °C for 2 hours, the composite film was properly affixed to the silver electrodes on the PET substrate as shown in figure 5.7. The sensor could detect the hydrogen ions in the sample solution and the resistance between the electrodes changed after immercing the sensor in different pH levels, although the sensor's stability and sensitivity was not that much high.

5.7 Increasing the weight percentage of PANI (ES) in the composite

In the sixth approach:

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 5.2 μl of A composite solution consisting of 40 (wt%) of aqueous SWCNT/SDS solution and 60 (wt%) of PANI (ES) solution in NMP solvent drop-casted on the silver electrodes.
- finally the sensor cured for 1 hours at 90 °C.

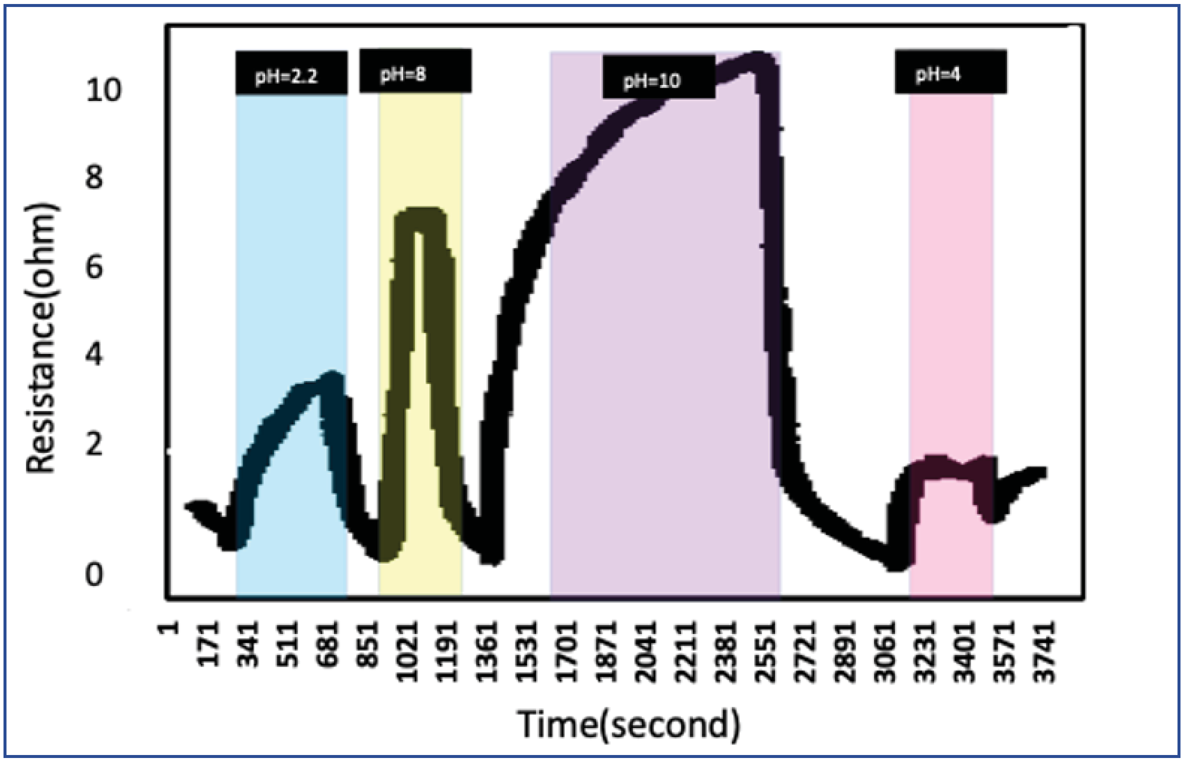

Figure 5.6 Electrical resistance changes after dipping the sensor in the pH 10,8,4,2.2

5.7.1 Result and discussion

Like the other approaches we discussed about them before, we measured the the electrical resistance changes in the different acidic and basic sample solutions by SMU exhibited in figure 5.8. After trying different ratio of PANI (ES) and SWCNT in our composite, in this approach, we reached to the best ratio of PANI((ES)60 (wt%)) and 40 (wt%) of aqueous SWCNT/SDS solution, after testing the sensor in different sample solutions we found out that the Stability and sensitivity was increased. So we decided to try different ratios of our sensetive material in the next approaches.

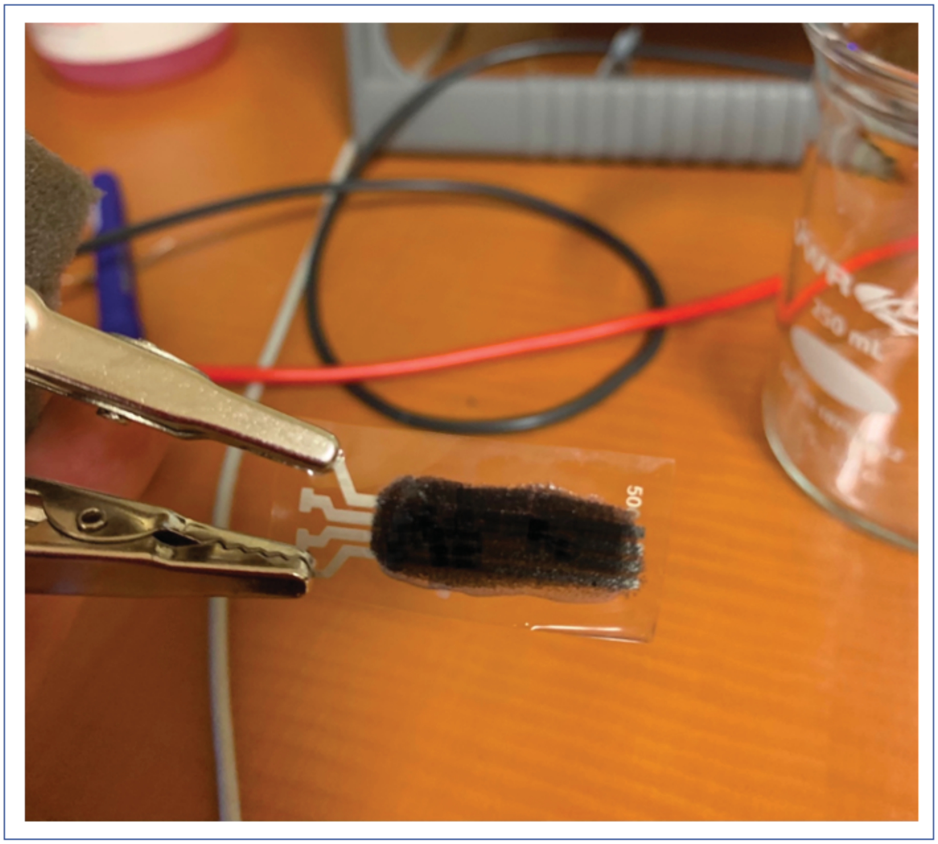

Figure 5.7 Composite film and silver electrodes on the substrate

5.8 Applying an aditinal layer of PANI (ES)

- First, Ag electrodes screen-printed on the pre-cleaned polyethylene terephthalate (PET) substrate.
- Then electrodes were cured at 120 °C for 2 hours.
- 5.2 μL of composite solution consisting of 40 (wt%) of aqueous SWCNT/SDS solution and 60 (wt%) of PANI (ES) solution in NMP solvent drop-casted on the silver electrodes.
- The sensor cured for 1 hours at 90 °C.
- 0.1 μL of PANI (ES) solution in NMP solvent drop-casted on the SWCNT/PANI composite film.
- The sensor cured for 1 hours at 90 °C.

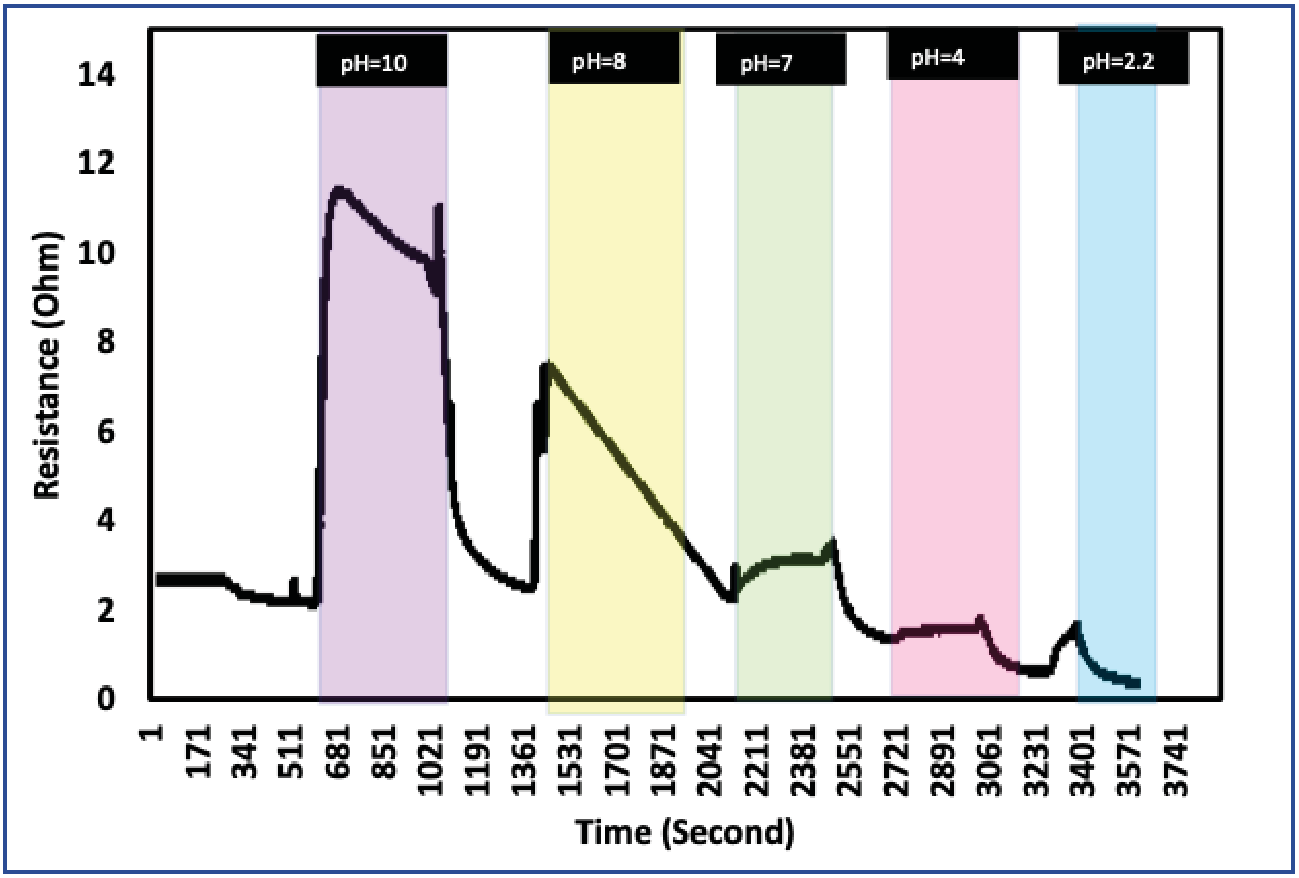

Figure 5.8 Electrical resistance changes after dipping the sensor in the pH 10,8,7,4,2.2

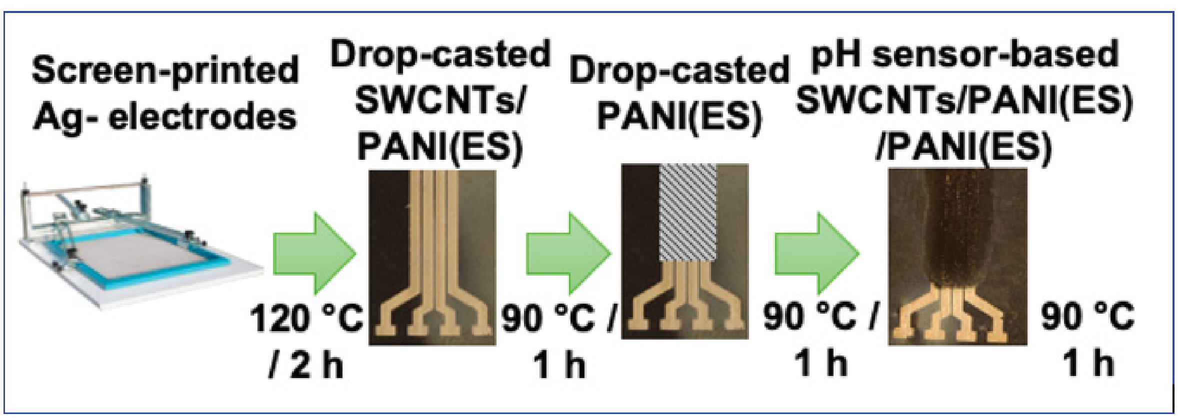

Figure 5.9 Final fabrication process

5.8.1 Final Result and discussion

In this approach, an additional layer of PANI (ES) solution was drop-casted on top of the cured SWCNTs/PANI (ES) layer with a final curing step at 90 0C for 1 hour, resulting in a SWCNTs/PANI (ES)/PANI (ES) active layer as shown in figure 5.9. Like the other approaches, we measured the the electrical resistance changes in the different acidic and basic sample solutions by SMU presented in figure 5.10:

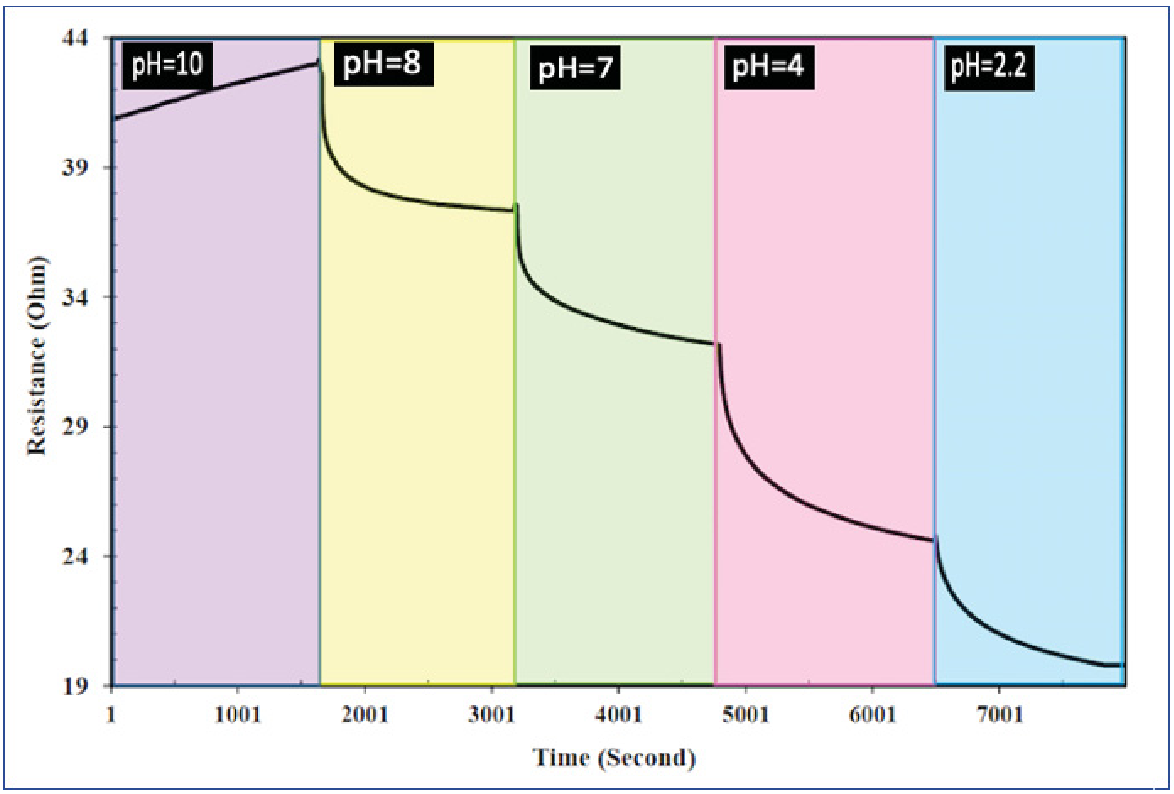

Figure 5.10 Electrical resistance changes after dipping the sensor in the pH 10,8,7,4,2.2

Figure 5.11, 5.12 and 5.13 show SEM micro-graphs of the sensors' surfaces made from SWCNT aqueous solution, SWCNT/PANI (ES) nancomposite and SWCNT/PANI (ES)/PANI (ES) nanocomposite films. Firstly, sensors made of pure SWCNTs showed poor adhesion between the SWCNTs and the Ag-electrodes. By using a SWCNT/PANI (ES) nanocomposite film, there was an improvement in the microscale porous morphology, with the SWCNTs distributed over the sensor's surface. This resulted in a conductive network structure composed of connecting micron-sized nanotubes.

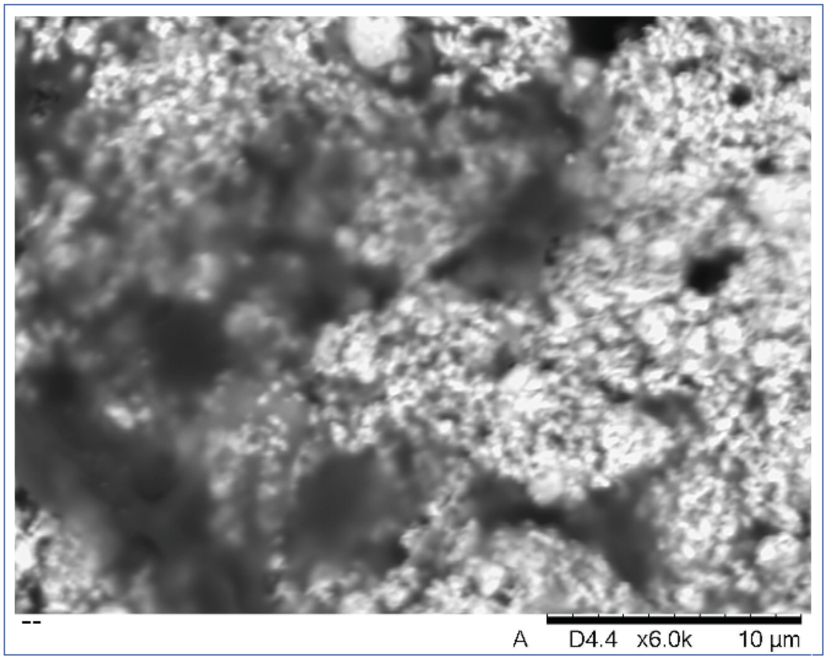

Figure 5.11 Pure SWCNT aqueous solution

However, the film exhibited separation during drying, resulting in sensors with a non-uniform sensing layer. An additional PANI (ES) layer drop-casted on top of the first SWCNT/PANI (ES) film provided a better coating of the sensor's surface with PANI (ES), producing a more uniform and thick porous film. The final sensor is indicated as SWCNT/PANI (ES)/PANI (ES).

Compared to pure PANI (ES) and SWCNTs sensors, the SWCNTs/PANI (ES) nanocomposite sensor showed better pH sensitivity while reducing the response time from over 10 min to 400 s. The SWCNTs played an essential role in forming a conductive network supporting the PANI (ES) which provided an abundance of active amine groups that can protonate/deprotonate. Consequently, the electrical charge transferred faster throughout the SWCNT/PANI (ES) nanocomposite film, enhancing the response time for sensors. Further improvements in the sensing performance were observed by drop-casting an additional PANI (ES) layer on top of the pre-cured SWCNT/PANI (ES) nanocomposite film. The additional PANI (ES) layer

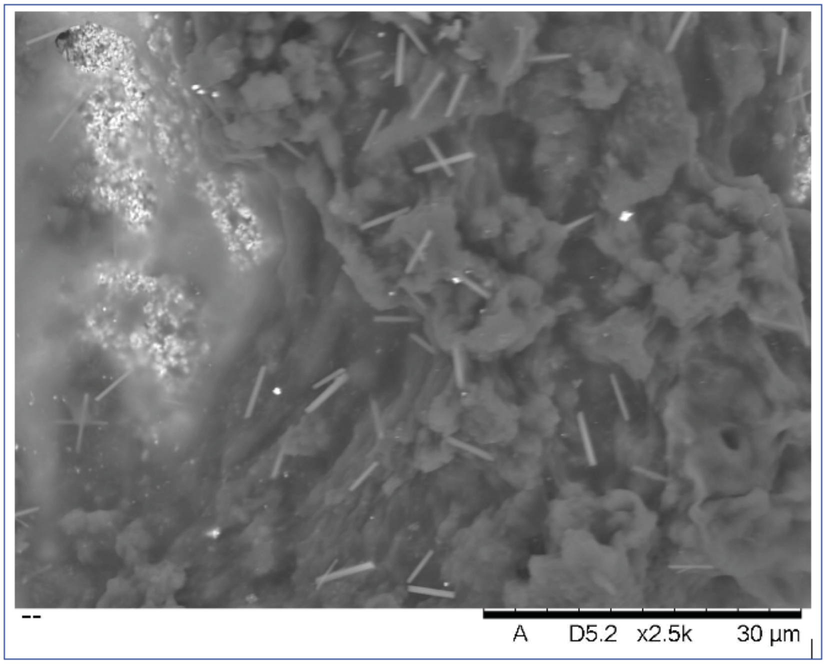

Figure 5.12 SWCNT/PANI (ES) nancomposite

created a more uniform and robust layer, leading to a significant reduction in response time from 400 s to 70 s for the SWCNT/PANI (ES)/PANI (ES) sensors. Furthermore, the signal stability of the sensors increased. It is important to note that the sensitivity of our SWCNT/PANI (ES)/PANI (ES) sensors is comparable or superior to other reported pH sensors such as the carbon nanotube-based and the polyaniline-based chemiresistive sensors (Emami *et al.*, 2021).

indicates the resistance change of the chemiresistive pH sensor after exposure to different pH solutions at room temperature. The sensors were not cleaned between subsequent pH tests. As previously discussed, the decreasing pH value resulted in a decreasing electrical resistance. The chemiresistive sensors showed a high sensitivity of 2.72 /pH with a response time of 70 s. Moreover, by plotting the steady state resistance values, figure 5.14 shows high linearity of the chemiresistive sensor over a wide pH range between 2 and 10 (Emami *et al.*, 2021).

Finally, figure 5.15 indicates a reversible and repeatable sensing mechanism after exposing the sensor in alternating acidic and basic solutions over several cycles.

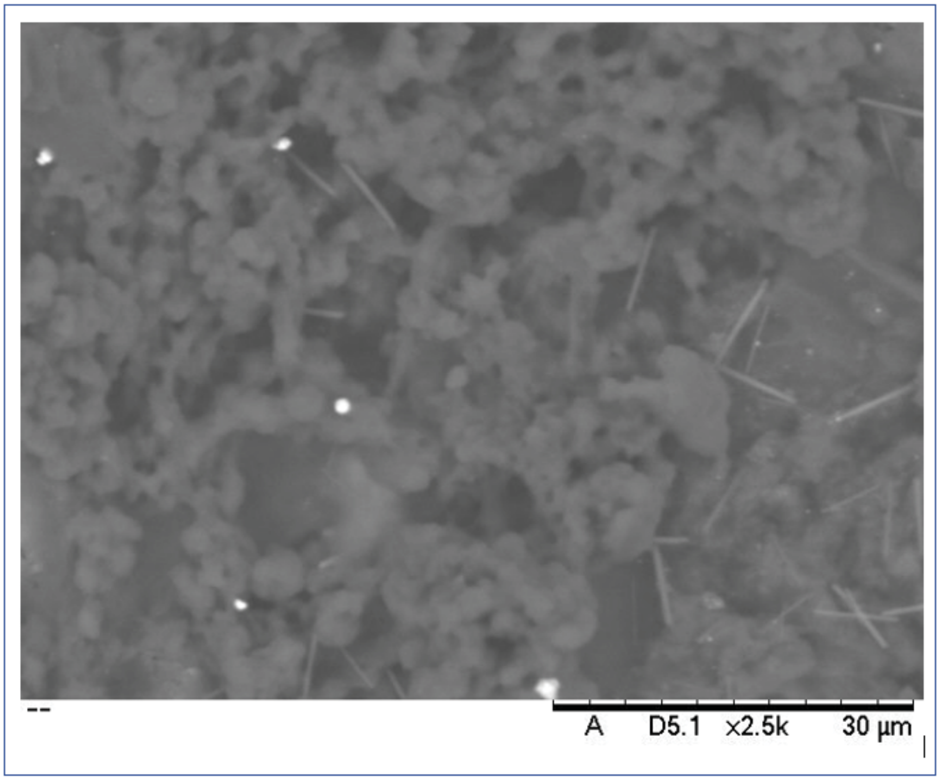

Figure 5.13 SWCNT/PANI (ES)/PANI (ES) nanocomposite films

Due to PANI (ES) being a p-type semiconductor, increasing the concentration of holes during protonation in acidic solution resulted in increased conductivity of SWCNT/PANI (ES). In an acidic environment, positively charged carriers induced into SWCNT's surface demonstrated dominant hole transport when C—O bonds adsorb H+. The opposite occurs in an alkaline envoironment. Finally, increasing pH values reduced the pH sensitivity of pure SWCNTs sensors. To overcome this issue, PANI (ES) was introduced and has more H+ available to lose by immersing the nanocomposite in solutions with higher pH values (Emami *et al.*, 2021).

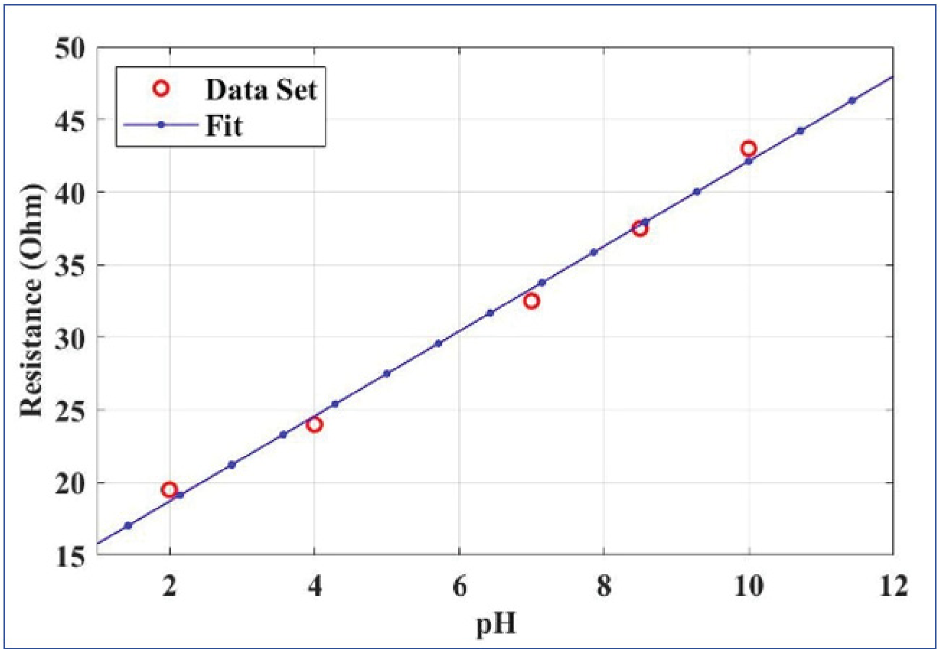

Figure 5.14 High linearity of the chemiresistive sensor

5.9 Conclusion

In this chapter different approaches were examined, some parameters remained the same, such as silver electrodes printed on a PET screen as well as the curing temperature of the electrodes. In these approaches, items such as the method of film formation on silver electrodes, SWCNT and PANI ratios, as well as the final curing temperature of the sensors were optimized. To achieve the desired result, the ratio of PANI to SWCNT should be higher, and also an extra layer of PANI can increase the sensitivity and stability of the sensor. We used PANI (EB) and PANI (ES) were used in these examinations. PANI (ES) showed better sensitivity than PANI (EB) due to its available hydrogen ions that can loose in basic solutions and finally the temperature and the length of time the sensor remains in the oven for curing are optimized to prevent the composite film from breaking on the PET substrate.

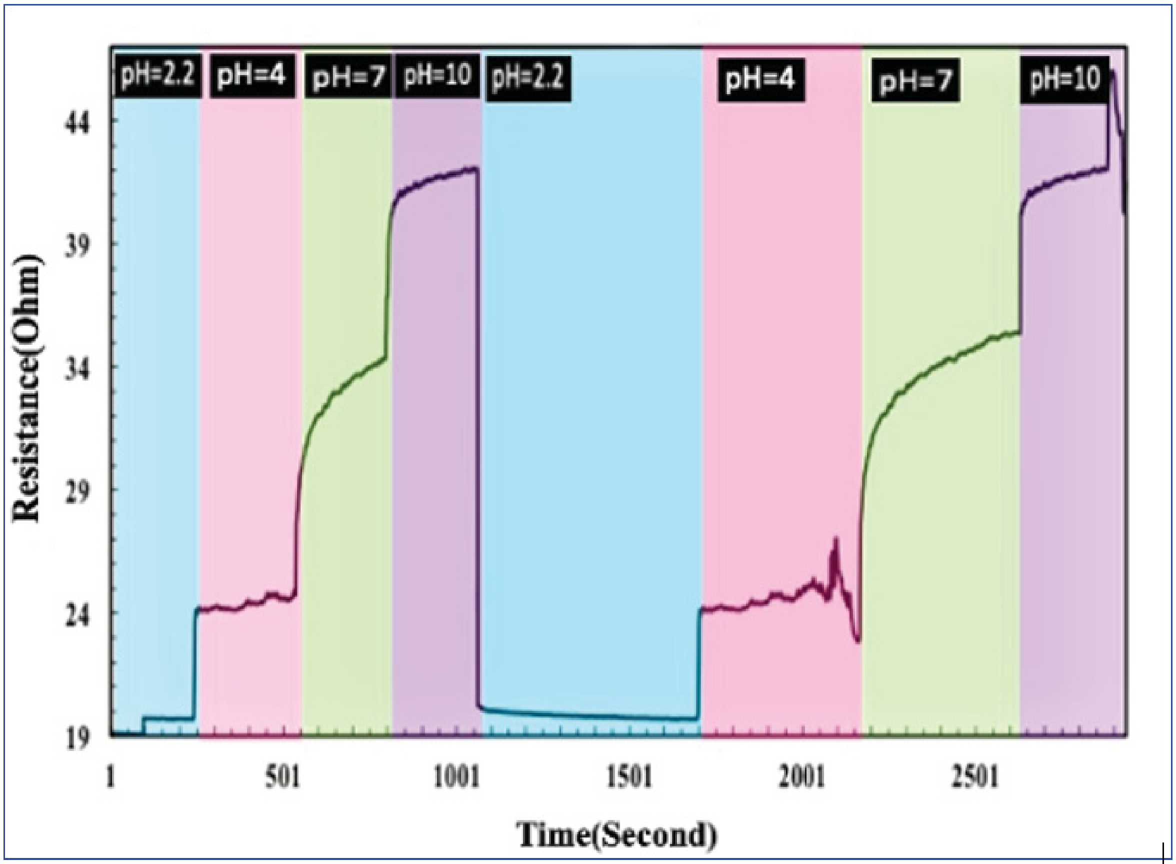

Figure 5.15   Reversible and repeatable result of the chemiresistive pH sensor

CONCLUSION AND RECOMMENDATIONS

An optimized SWCNT/PANI (ES)/PANI (ES) chemiresistive pH sensor on PET substrates was presented in this project. pH measuring and monitoring are widely used for diverse IoT applications such as food packaging, medical diagnosis, biological sensing, water quality monitoring, and agricultural optimization. In particular for the medical field, smart bandages with embedded pH sensors can be vital in determining the health of damaged tissue cells and the status of the bandage itself by detecting the pH levels of the fluid analytes excreted from wounds. Healthy skin pH is acidic between 4-6 pH, while many human pathogenic bacteria can grow only in pH values over 6. Therefore, proper monitoring of skin pH will add value to patients and health care providers in identifying the onset of infection. Traditional bandages can not detect the state of the wounds by detecting different parameters such as humidity, tempreture and pH. Smart bandages with embeded sensors can assess the state of the wound and the bandage by itself. pH level is one the most important parameter which is a detector of wound healing stages. These bandages needs to be flexible, easy to fabricate, cost effectiv and easy to test. Existing pH sensors such as ISFETs and potentiometric pH sensors are fragile and needs reference electrode. Chemiresistive sensors operate due to the change in electrical resistance in the presence of a chemical target. Different materials such as metal oxides are used as the hydrogen sensetive material but they can detect a limited range of pH level, shows low accuracy and they are not suitable for biomedical applications. Carbon nanotubes are a proper group for sensing hydrogen ions. There 4 types of polyaniline based on their conductance. Based on our results the most effective kinds of PANI is emeraldine salt(PANI (ES)) which is suitable to be used in chemiresistive pH sensors. Although PANI (ES) is not fully oxidized, its conductivity is more than PANI (EB) and has more available site to be oxidized than the fully oxidized form of PANI (ES). While brittle sensors were prepared from pure SWCNTs, the addition of PANI (ES) not only enhanced the SWCNTs adhesion to the PET substrate, but also provided an abundance of active amine groups, leading to elevated SWCNT/PANI (ES) sensor sensitivity for pH detection.

Coating the SWCNT/PANI (ES) layer with an additional PANI (ES) layer resulted in a uniform and thick porous film, further improving sensor sensitivity and response time. Supported by the conductive SWCNT network, sensors were observed to have a high pH sensitivity of 2.72 /pH, a fast response time of 70 s, and high linearity in the pH range between 2 and 10. Finally, the as-fabricated sensors of SWCNT/PANI (ES)/PANI (ES) showed better signal stability and repeatability. The size of this sensor is small and it is designed for smart bandage. According to the application that may have in the future, this size can be changed. Due to its low-cost fabrication, small size and flexibility, the sensor is a good candidate for future smart bandage and wound analysis applications.

6.1 Recommendation for future

In this work we used the powder form of PANI and CNT which dispersed in their proper solvents. The desired dispersion of our material was liquid and they have a very low viscosity, by using the materials with higher viscosity, Our fabricated sensor can be built in a fully printed form by screen printing process or other fabrication technique methods such as aerosol jet printing method. By adding different materials to the dispersion we can have the material with high viscosity. By utilizing different ratio and optimizing existing hydrogen sensitive materials the sensitivity of the sensor can be increased. in this work we used PET substrate, in the future the desired film can be printed on the other substrates such transparent bandage.

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