Electrically Conductive Cotton Textile and Its Applications

Sicong Liu  
*The University of Western Ontario*

Supervisor  
Jun Yang  
*The University of Western Ontario*

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Abstract

Electronic textiles (e-textiles) have been considered as important applications in wearable electronics, which can combine the functionality of smart electronic devices with the comfort and flexibility of stylish clothing. Herein, we have successfully prepared a conductive textile via electroless deposition onto cotton textiles by using a three-step treatment process. The cotton textiles are first dipped in P4VP-SU8 solution to form a uniform layer for the subsequent absorption of silver ions. Then, the cotton textiles are immersed in silver nitrate solution in preparation for the next step electroless deposition. The sheet resistance can be as low as 0.05 $\Omega \text{sq}^{-1}$. Two sensors were made based on the copper coated cotton textiles. One is flexible pressure sensor, the other is ECG sensor. Both sensors performed well, proving this method is a promising candidate for applications in the fabrication of functional textile-based wearable devices.

Keywords

E-textiles; Electroless deposition; Pressure sensor; ECG sensor
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Chapter 1

1 Introduction

1.1 Electronic Textiles

1.1.1 Definition

Electronic textiles, or e-textiles, are textiles that are integrated with electronic devices. They are also called as smart textiles or intelligent textiles. Undoubtedly, these textiles refer to a large field of products that are beyond the usefulness and functionality of daily fabrics, which have the power to interact with the environment and user. Textiles are new and attractive platforms for integrating advanced technologies, especially nowadays when human interaction with technologies is highly encouraged. The appearance of e-textiles can be dependent on the development of new and smart materials that are capable of achieving a variety of functions, found in the daily electronic products we use. They can have the functions like communication, power transmission, sensing or harvesting energy while keeping their original feel and mechanical flexibility.

According to the working principle of e-textiles, they can be classified into two types. The first one is just textiles with electronic devices like light emitting diodes, resistance and traditional batteries attached on the surface. This type is a little bit far away from wearable electronics, because stretchability, flexibility and other advantages are lost. Another type, electronics are directly integrated into the textile fiber or fabrics. Both inactive elements like pure metal wires and active elements like transistors or diodes can be contained in the e-textiles.

1.1.2 Applications of E-textiles

E-textiles combined with wearable electronics have been a very hot research field
recently. E-textiles have different functions when integrated with different components. Passive smart textiles are only able to sense the environment according to sensors. The fabric sensors can be used for electrocardiogram (ECG) [1], electromyography (EMG) [2], and electroencephalography (EEG) [3] sensing; fabrics containing thermocouples can be used for sensing temperature [4]; luminescent elements incorporated in fabrics can be used for biophotonic sensing [5]; shape-memory fabrics can detect motion and can be combined with EMG sensing human behavior [6]. The textile coated with carbon materials can be used to help monitor or detect specific environmental features like toxic gas, humidity or other parameters [7, 8]. To some active textiles, active functionality could be added including power storage or generation [9], radio frequency (RF) functionality. Power generation can be generated through piezoelectric [10] elements that can collect energy from motion [11]. Active human interfaces include input devices and display devices. Capacitive patches can be used as push buttons and shape-sensitive fabrics can record pressure and motion.

Fig. 1-1 shows the smart shirt and intelligent biomedical clothes developed by European funded projects MY HEART. The fabric sensors implemented with the wearable systems can be used for health monitoring of body parameters such as heart beat rate and respiration rate. The fabric sensors were made by using commercial stainless steel threads twisted around a standard continuous viscose or cotton textile yarn. This system was designed for collecting risk factors to support the human with data to fight against major cardio-vascular diseases and help us avoid a heart attack. Therefore, it can provide the necessary motivation for the new life styles.

Fig. 1-2 illustrates the silver-coated textile electrodes integrated into the smart jacket prototype [12]. The jacket chest is open and the fabric electrodes are on the back for clinical observation. The jacket also has a hat for protecting eyes. The six textile electrodes are distributed in different positions of the jacket, which can effectively decrease the motion artifacts. This design also allows free movement, especially for babies who cannot control themselves, which is greatly appreciated by parents and doctors.
Figure 1-1 Wearable instrumented garment for monitoring vital signs. (Copy from [2])

Figure 1-2 A prototype of the smart jacket (left) and a baby mannequin wearing the smart jacket inside the incubator (right). (Copy from [12])
1.1.3 Different Coating Methods and Materials of Conductive Textiles

1.1.3.1 Different Coating Methods

These smart materials can be integrated with the textile structure by different technologies (Fig. 1-3). Among those, there are embroidering [13], sewing, non-woven textile, knitting [14], weaving [15], making a spinning [16], braiding [17], coating/laminating [18], printing [19] and chemical treatments [20]. This thesis mainly focuses on different coating methods and different materials.

Figure 1-3 Different kinds of textile/fabric manufacturing and treatment (a) Embroidery; (b) sewing; (c) weaving; (d) non-woven; (e) knitting; (f) spinning; (g) braiding; (h) coating/laminating; (i) printing and (j) chemical treatment. (Copy from [21])

Among these methods, coating is the most commonly-used method for fabricating electrically conductive textiles. A textile coating is essentially a new layer attached to a textile original structure, similar to spreading butter on bread. Textile coatings are used to add or alter the functionality of the textiles.
Dip coating, also called pad coating, is a dipping procedure where excessive coating formulation is squeezed out of the fabrics by rollers. Fig. 1-4 illustrates how dip coating works. This pad-mangle coating process can be deemed as a combination of dip coating and a forward two-roll coating process. This method can make the coating penetrate into the interstices in the fabric and between the fibers in the yarn. This coating method has the advantages of covering the entire fabric, while most other coating methods can only make one-side coating. The amount of applied materials on the fabric is mainly determined by the coating viscosity as well as the speed the fabric moves through the coating solution. The roll coating will be affected by the roll speed, nip pressure and coating viscosity.

![Figure 1-4 Schematic illustration of pad-mangle coating. (Copy from [22])](image)

Screen printing is the most common printing methods in the textile industry. It is more efficient and faster when compared to other methods. The basic mechanism behind screen printing is that the printing formulation is pressed through a screen onto the substrate, shown in Fig. 1-5. Usually, the screen is printed with the opposite of the desired pattern. As can be foretold by their names, screen printing uses a cylindrical screen, which is made of nickel. In industry, the textiles rest on a rubber mat that forwards the fabric under the rotating screen. As the friction is not high, this method is suitable for more delicate
and stretchable textiles with uneven surfaces.

**Figure 1-5 Schematic illustration of flat-bed screen printing.** (Copy from [23])

Knife coating, also known as direct coating, is also one of the widely used techniques in the textile industry. The working mechanism is really simple. A blade smears out a thickened polymeric formulation across a moving textile substrate. If the substrate rests on a roller below the blade, this method is also called knife-over-roll method, illustrated in Fig. 1-6. As the fiber moves forward, it is scraped by the knife and the surface is evenly spread with the polymer resin compound. There are many factors that may affect the coating quality, like blade angle, coating speed and shear viscosity. The amount of coating materials relies on the concentration of solution [24].

**Figure 1-6 Schematic illustration of knife-over-roll coating.** (Copy from [25])
1.1.3.2 Different Coating Materials

Among the many possible conductive materials, carbon, metal and conductive polymers are three main materials used on the surface of textiles.

1.1.3.2.1 Metals

Initially, thin wires of metals were added to textiles for decorative purposes. It was not until the development of vapor deposition techniques in the 1960s that metals were more widely used in textile industry for their electrical conductivity. Copper and silver are two mostly used conductive metals, and other metals like tin, steel, nickel, aluminum, gold are also used. Despite their shortcomings of lack of flexibility, high cost, they are still the best material candidates for applications where high conductivity is required. Common techniques for coating metals include electroless plating, sputtering, and dip coating.

With development of nanotechnology, metallic nanowires are applied in fabricating conductive textiles. For example, Goldthorpe’s group has created electrically conductive textiles by combining silver nanowires and fabric threads using a dip-coating method [26]. They demonstrated that polyester, nylon and cotton threads all can be made conductive by coating their surfaces with random networks of solution-synthesized silver nanowires. They achieved a resistance per unit length of $0.8 \, \Omega \, \text{cm}^{-1}$, and can vary the resistance through the density of the nanowire coating. The conductivity did not vary after repeated bending.
1.1.3.2.2 Carbons

Carbon materials of different structures have diverse properties including conductivity, varying from insulator diamond to conductors like carbon black, graphene and carbon nanotubes (CNT).

The carbon atoms of carbon nanotubes form a cylindrical nanostructure whose diameter is only nanometer scale. The length-to-diameter ratio can be as large as 132000000:1. Carbon nanotubes have been applied in various fields of materials science and engineering, such as electronics, nanotechnology and optics because of its unique properties. The electron mobility of a single carbon nanotube can be higher than 100 000 cm²/V • s [27].

However, despite the fact that the resistance of a single CNT is quite low, when two
carbon nanotubes overlap each other, the junction resistance is very high between 200 kΩ - 20 MΩ, which makes the conductivity of CNT network low when coating on the textile surface. Besides, carbon nanotubes can be either semiconducting or metallic. Although the metallic ones have higher conductivity, it is not possible yet to synthesize metal-only carbon nanotubes but mixtures of metal and semiconductor ones.

Cui’s group has made a stretchable, porous, and conductive textile using an extremely easy “dipping and drying” process using single-wall carbon nanotube ink [28]. The conductivity is 125 S cm⁻¹ and sheet resistance is less than 1 Ω/sq. This conductive textiles show outstanding flexibility and stretchability, demonstrating strong adhesion between the SWNTs and the textiles.

![Figure 1-8 Schematic of SWNTs wrapping around cellulose fibers to form a 3D porous structure. (Copy from [28])](image)

Haddon’s group developed a chemical processing method which allows continuous spinning of single-walled carbon nanotubes on nylon fiber through in-situ polymerization. The process results in a uniform dispersion of the SWNTs, and the existence of the graft copolymer enhances the polymer/SWNT compatibility while strengthening the interfacial interaction between the nanotube and matrix [29].
Besides carbon nanotubes, graphenes are two-dimensional materials with a very thin layer of carbon atoms bonded together in a hexagonal honeycomb lattice. Graphene can have very high conductivity when doped with other materials.

Samad et al. have discovered that a variety of textiles can be cladded with chemically modified graphene through a three-step method to generate electrical conductivity, illustrated in Fig. 1-9 [30]. Electrical conductivities of 13 and 4.5 S cm\(^{-1}\) were obtained for aramid and nylon fibers respectively. The coating is so uniformly distributed that the washing or sonication cannot destroy it. Donghe et al developed a graphene coated nonwoven, which showed good conductivity and potential applications in wearable sensors [31]. They used a simple brush-coating and drying technique for the fabrication. A piece of NWF was dipped into graphene oxide (GO) solution and then reduced in HI acid, shown in Fig. 1-10. Xiang et al. have tried to coat Kevlar fibers with graphene nanoribbons via spray-coating. The fiber had conductivity of 20 S/cm [32].
1.1.3.2.3 Conductive polymers

Polymers are normally insulating, but it was not until the discovery of conductive
polyacetylene with iodine doping by Shirakawa in the 1970s that it was realized that several other polymers like polyaniline, polypyrrole and polythiophene etc. could be doped to be conductive as well. The chemical structures of these common conductive polymers are shown in Fig. 1-11.

Irwin’s group prepared a conductive polymer-coated threads as electrical interconnects in e-textiles [34]. They cast silk fibers with the ionomer mixture poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS; 1:2.5, w:w) by a dip-coating process. They proved that PEDOT: PSS is a superior material for fabricating conductive textiles. They also tested this conductive textile as an interconnect in circuit. Bangting et al successfully prepared a conductive textile via covalently grafting polyaniline (PANI) onto cotton using a multi-step treatment process. Moreover, the conductive and insulating properties of this textile can be conveniently tuned by alternately immersing in alkaline or acidic solution. This conductive textile shows excellent advantages of remaining its conductivity in the washing test [35].

![Chemical structures of conductive polymers](image)

**Figure 1-11 Chemical structures of these common conductive polymers. (Copy from [33])**
1.2 Basics of Cardiac Physiology

Before discussing the epidermal ECG sensor, it is significant to understand the basics of the electrocardiogram (ECG) itself. The word *electrocardiograph*, abbreviated as an EKG or an ECG, stems from Greek words: electro, because it has something to do with electric activity; kardia, referring to “heart” and graph meaning “to write”. Therefore, from the meaning of the word itself, electrocardiograph means recording the heart activities using the electrical signals coming from a human body. The electrical signals are recorded by utilizing electrodes attached onto the skin. Many types of damage to the heart can be easily detected with an ECG. The ECG wave form allows us to infer important data about the electrical activity connected with the heartbeat, so it is very valuable for assessing the patient’s heart health and cardiac rhythm.

Usually, an ECG signal is represented by a graph. In the graph, the x-axis represents time and y-axis represents voltage. This graphical representation (ECG) can be presented in two ways, either displayed on a monitor or printed on a paper. The device used for recording and printing the ECG on paper is called electrocardiograph, while the device which displays the ECG on a screen is called monitor or cardiac monitor. During a clinical diagnosis, the signal amplitude and the time scale are both very significant. In the past, a specially designed paper filled with small squares is utilized when printing ECG signal. The speed of printing must be unified with the analysis.

When the atrial and ventricular muscle is still, extracellular ions are in a positive ionic state and intracellular ions are in a negative ionic state, so the polarization state is formed. The polarization state collapses once the cardiac fibrillation happens, which is called "depolarization" process. Heart can be regarded as a power supply during the whole process, as depolarization and repolarization cause biological potential changes, which makes the source voltage in the heart generate change, as shown in Fig. 1-12. By transmitting the conductive tissues and fluids around the heart to the body surface, the body surface will have different potentials over time, so the electrical potential signal can be collected by ECG monitoring device.
A complete cardiac rhythm is also called as a “sinus” rhythm due to the origination in sinoatrial node (S-A node). The malfunction of this normal sinus rhythm is referred as arrhythmias. “Pacemaker” cells trigger each heart beat in the S-A node. Normally, action potentials are generated at 60-100 beats per minute by these cells. When the action potentials propagate through the myocardium in a predefined way, the action potentials depolarize, making muscle tissue contract. After leaving the S-A node, the action potentials depolarize the heart’s two upper chambers called as the atria, and then travel to the atroventricular node (A-V node). This node exists between the two lower chambers of the heart called as the ventricles and the atria, which acts as a backup pacemaker at a lower rate of 40-60 beats/min. The electrical impulses are postponed by the A-V node, slowing them down by about 120 ms to provide the atria sufficient time to eject the blood into the ventricles before it contracts. After leaving the A-V node, they keep moving to the left and right bundle branches. After the ventricles contract and depolarize, the cycle restarts with another impulse from the S-A node. This is a complete cycle how an ECG impulse comes out [36].

Figure 1-12 An ECG waveform is composed of action potentials originating in different areas of the heart. The ECG waveform recorded at the skin is the superposition of these different action potentials. (Copy from [36])
A normal myocardial motion has a fixed potential fluctuation cycle, and the waveform curve is regular within each cycle. A complete ECG diagram consists of P wave, QRS wave, and T wave, as shown in Fig.1-13, where the P wave corresponds to the atrial depolarization wave; QRS wave corresponds to the ventricular depolarization wave; T-wave corresponds to the ventricles repolarization wave. One heart beat period is defined as the time difference between two continuous P waves. When the heart is not working properly, the abnormal changes in the electrical activity of the heart can be immediately reflected in the electrocardiogram [37]. This immediate reaction of the electrocardiogram to the cardiac activity can provide a reliable intuitive basis for doctors to aid in the diagnosis of myocardial infarction, ventricular hypertrophy, arrhythmias, heart disorders etc.

![Figure 1-13 A 'Normal' ECG waveform. (Copy from [37])](image)

1.3 Introduction of Current ECG Sensors

1.3.1 The Principle of ECG acquisition

The purpose of connecting electrodes to the human body is to extract the bioelectrical
signal for subsequent processing. The electrical potential signal inside human body is transmitted through body fluids and tissue fluid in the form of ions transmission, but signal of the ECG monitoring device is transmitted by electrons. As a result, the signal acquisition part needs to transform the ion stream into a stream of electrons, so electrochemical reaction takes place at the interface of the skin and the electrode [36], the principle is shown in Fig. 1-14.

![Electrochemical reaction diagram](image)

**Figure 1-14** The electrochemical reaction at the interface of skin and electrode.

(Copy from [37])

Traditional ECG electrodes are Ag/AgCl electrodes with a layer of conductive gel, where Ag/AgCl acts as conductive metal and Signagel acts as electrolyte. The reaction principle is: the metal electrode at the interface which is oxidized to positive ions flow into the electrolysis liquid, while the electrons left become electronic carrier in the electrode. The negative ions coming to the interface are reduced into neutral atoms and release free electrons to the electrode. This is the process where conductive ions in the electrolyte are converted into conductive electrons in the metal electrode.

Just two electrodes can be used to measure the ECG signal. These electrodes are normally put on the both sides of the heart on the chest where the signal is most significant. For a simple measurement, two electrodes are enough to obtain the heart rate. For more precise and accurate measurements, two electrodes are not sufficient. The use
of different combination of electrode pairs, which are called leads, spread over the human body, which helps to detect the cardiovascular disease better.

The position for placing the electrode, electrocardiogram measuring method and test principles are shown in Fig. 1-15 in a way that bipolar leads are connected. $E_s$ is the source of heart signal potential, and $E_c$ is capacitively coupled to the power supply potential. $Z_1$, $Z_2$, $Z_g$ are the skin impedances at the interface.

![Figure 1-15](image)

**Figure 1-15** (a) Electrode connection for measuring ECG signal (b) The equivalent circuit of ECG measurement. (Copy from [38])

### 1.3.2 Species of ECG Electrodes

Various kinds of ECG devices have been developed to record and detect the signal. Measuring the ECG signal is one of the four methods to detect and diagnose heart diseases in an objective way, and also in a convenient and important way. The first device was invented in the 1880s. Understanding the mechanism of the ECG signal and finding methods to analyze it were developed really quickly during the following years. Owing to the development of analog circuit devices, the tiny voltages were produced by human heart can be measured. In the year of 1901, a breakthrough in measuring ECG signal was discovered by Willem Einthoven using a string galvanometer. He used this string galvanometer to study the mechanism of a human heart function. He used the alphabetical letters to describe the various deflections in the ECG signal.
The current ECG electrodes in use can be classified based on the principles of electrode signal acquisition, whether the electrode is dry or wet, the power source and whether the electrode is reusable or intended for one-time use. There are three types of ECG signal acquisition, including resistive, capacitive and inductive. Depending on the power source, the electrode can either be passive or active.

1.3.2.1 Metal Electrodes Used in the Clinic

Currently, the most commonly used clinical electrode structure is disposable Ag/AgCl electrode. A small disk is embedded in one side of a larger plastic foam disc. The plastic foam has a metal clasp on the other side which is connected to the silver-plated disc. When in use, the connection line connects with the metal clasp, while the silver-plated disc is coated with a layer of conductive gel. The conductive gel will gradually become dry and not suitable for repetitive measurements, shown as Fig. 1-16. This kind of electrode is irritating for a long period use. As a result, the electrodes need changing every day in order to avoid allergic skin reactions. What’s worse, these gel electrodes are attached to human skin using adhesive gels or tapes, which may also cause chemical or mechanical irritation, but the main discomfort is caused by stripping a thin layer of skin when removing if the tape is too sticky. Moreover, because of the high impedance of the electrode, stratum corneum is usually abraded to decrease its thickness.

*Figure 1-16 Commonly-used Disposable ECG Electrodes. (Copy from [38])*

Another kind of limb electrode is also commonly used in hospital, the appearance of
which is bent into a flat metal plate columnar segment. A connector is placed near the outer surface of the electrode at one end of the joint to connect the ECG lead wires. A column near the center on the same side is often used to connect a fixed electrode onto the arm or leg, as shown in Fig. 1-17. This electrode is commonly made of nickel electrode-silver alloy. A layer of conductive gel electrolyte will be coated on the rough surface before the signal acquisition.

In addition, there is an adsorption-type electrode, and it is just a metal plate electrode in another form. It is usually connected to chest used for short time ECG measurement. Without the aid of a bandage or sticky glue, it adheres to skin using negative self-pressure. It consists of a hollow cylinder, having one end connected to the hemispherical metal electrodes and the other end connected to the rubber ball. The hemispherical electrode is coated with conductive adhesive when used. Spherical shape electrodes are shown in Fig. 1-18.
Dry Electrodes

One kind of electrode that operates without gel or adhesion is called dry electrodes. However, the dry electrodes may result in the following problems: (1) the contact impedance is much larger than that of gel electrodes (2) the contact area may change due to its rigidness during measurement. There are various possible candidate materials eligible for dry electrodes: Rigid materials, like metals; Flexible materials, like rubber, foam or fabrics.

People have been trying the metals as dry electrodes, such as stainless steel, silver and aluminum. Some materials have been proven unsuitable to be used as dry electrodes, such as aluminum. Aluminum has the problem of oxidation caused by perspiration during long term use. Some studies have considered stainless steel as a good candidate. It not only has good performance, the price is also low compared to other metals. What these stiff electrodes have in common is that they can easily slip off the skin, causing a loss of contact between the electrode and skin.

The surface of human is not smooth plane. A reliable and stable contact between the ECG electrode and human skin is very significant for all kinds of electrodes. Rigid and solid material electrodes have the problem of motion artifacts due to two concerns: the absence
of electrode gel and unexpected movement of the electrodes on the skin. In order to overcome this drawback that the metal electrode cannot conformally contact with the skin, many scholars are trying to develop a variety of flexible electrodes. Flexible and soft electrodes adapt to the human body shape and reduce motion artifacts. What’s more, the better adhesion and flexibility also enhance the contact area and reduce impedance and motion artifacts.

There are a variety of flexible materials. As shown in Fig 1-19, this new flexible electrode use PDMS as base materials, gold foil deposited with titanium as conductive element. It can be worn on your wrist with much convenience [38]. The electrode in Fig. 1-20 is developed by the Wacker company. In their design, they use the conductive rubber catalyzed by Pt as base materials and conductive element [39].

![Figure 1-19 PDMS based dry electrode. (Copy from [39])]()

![Figure 1-20 Dry electrode made of conductive rubber and integrated into a garment with shielded cable. (Copy from [39])]()}
1.4 Introduction of Flexible Pressure Sensors

Pressure, which is a force applied to the area over which it exerts per unit square, is everywhere in our daily life. The earth has gravity, even inside our human bodies; various pressures are generated in physiological activities, like intraocular pressure, blood pressure [40, 41].

A lot of progresses have been achieved in electrical sensing techniques and the development of organic electronics has contributed to the development of flexible pressure sensors, which have the advantages of low cost, flexibility and the ability to be compatible with large-area processing techniques. One of the many attractive applications of pressure sensors is mobile monitoring in medical diagnosis and personal health care. After years of development, a lot of functional materials have been explored for different sensing applications. Preparation of single pressure sensors with high sensitivity and combination of integrated circuits has been realized.

1.4.1 Categories of Pressure Sensors

The typical pressure range produced by human behavior like human body circulation and object operation are low-pressure (<10 kPa) and medium-pressure ranges (10-100kPa). The pressure sensors, which have the above pressure range, are of significance in various applications like human-machine interfacing devices, wearable health care systems. According to the paper [41], the pressure sensors are usually divided into four categories.

To understand different pressure ranges and the related sensing devices better, we divide pressures below 100 kPa into four ranges: ultra-low pressure (< 1 Pa), subtle-pressure (1 Pa-1 kPa), low-pressure (1-10 kPa) and medium-pressure (10-100 kPa) regimes as shown in Fig. 1-21[41].
1.4.2 Key Parameters of Pressure Sensors

A pressure sensor is a kind of transducer that can transform an exerted force into an electrical signal or other kinds of signals. To better evaluate pressure sensors, we need to know the essential parameters of pressure sensors. The key parameters of pressure sensors are limit of detection, sensitivity, response time, linearity and stability [41].

Sensitivity is undoubtedly one of the most significant parameters as it decides the effectiveness and accuracy of the device. The sensitivity is usually defined as $S = \frac{dX}{dP}$, where $X$ means derivative of output signal and $P$ means derivative of pressure, respectively [41]. The limit of detection, another very important indicator, refers to the lowest pressure that makes the sensor produce a significant signal change, which is also called the threshold value. Linearity refers to the phenomenon that the actual output of the sensor changes linearly with the operating scale [42]. The response of pressure sensor is more reliable and accurate in linear operation range. The response time is especially an important indicator in dynamic sensing devices, which is defined as the time range during the response process, from the moment when a pressure is applied to outputting a new stable signal. Another important parameter in wearable sensors is the operating voltage deciding the power consumption. Lowering the power consumption and decreasing the operating voltage is a trend in wearable electronics.
1.4.3 Transduction Mechanism

Currently, there are four types of pressure sensors, including piezoresistive [43], capacitive [44], piezoelectric sensors [45] and organic field effect transistors (OFETs) [46].

![Figure 1-22 Schematic images of transduction methods: (a) piezoresistivity, (b) capacitance, and (c) piezoelectricity. (Copy from [41])](image)

1.4.3.1 Piezoresistivity

Piezoresistive pressure sensors, whose resistance change according to mechanical deformation, have drawn increasing attention because of their great potential and widespread applications in human motion detection, health monitoring electronic skins. Sensors with good repeatability, high sensitivity and large scope are in great demand.

1.4.3.2 Capacitance

Capacitance means the ability to store electrical charge. Capacitance can be calculated by the equation $C = \varepsilon_0 \varepsilon_r S/d$, where $C$ is the capacitance, $\varepsilon_r$ is the relative static permittivity of the material between the plates, $\varepsilon_0$ is the electric constant, $S$ is the area of overlap of the two plates in square meters, and $d$ is the separation distance between the plates in meters. After a pressure sensor is fabricated, $\varepsilon_r$ is already determined, $S$ and $d$ can change by
applied pressure so the capacitance change [41].

1.4.3.3 Piezoelectricity

Piezoelectricity refers to electrical charges generated in certain types of solid materials (such as crystals and certain ceramics) in response to applied mechanical stresses. The piezoelectric effect is due to the occurrence of the electric dipole moments in solids. Piezoelectric sensors are mostly used in the measurement of dynamic pressures like the vibrations of sound [41].

1.5 Research Objectives

The main purpose of this research is to develop a novel fabrication process to fabricate conductive cotton textiles and also fabricate a sensitive flexible pressure sensor to monitor human motion and a textile electrode for measuring ECG signals. Based on our group’s advantage in printed electronics, electroless deposition is chosen as the main method for copper plating. A facile method of surface treatment before ELD process was discovered and is discussed based on in-situ cross-linked reaction of epoxy SU-8 with poly(4-vinylpyridine) (P4VP) and its strong reactive bonding ability with different pretreated substrates.

Chapter 1 provides introduction and background information for e-textiles and flexible pressure sensors as well as cardiac physiology and technical needs.

Chapter 2 introduces the detailed fabrication process. Parameters like P4VP concentration and ELD conditions are studied to optimize the whole process. Characterization of the properties of copper-coated textiles is also discussed.

Chapter 3 explores the potential applications of this conductive textile and introduces two sensors. Corresponding measurements and tests are conducted.

Chapter 4 summarizes the results and suggests the future research.
Chapter 2

2 Synthesis of Conductive Cotton Textiles

2.1 Overview of Electroless Deposition.

Electroless deposition can be defined as a deposition of solid phase of continuous coatings (films) or powders of metals, alloys, or compounds from aqueous or non-aqueous solutions or melts without an external current source [47].

In general, no external power is required for the electroless deposition. The coating film produced by electroless deposition is continuous and uniform, making this method very promising and attractive for different applications. Applications are related to different fields like energy, electronics, mechanical and aerospace, automotive and biomedical industries. Moreover, different kinds of substrates for metallization including ceramics, polymers and fabrics are developed [48, 49].

In electroless deposition, where the reduction of metal ions takes place, the presence of reducing agents is needed. There are mainly two types of electroless deposition of metals:

1. Displacement deposition

2. Autocatalytic deposition

For displacement deposition: When an active metal (M₁) is immersed into a solution containing metallic ions (M₂⁺) of a less active metal(M₂), reduction of these ions takes place according to the reaction below:

\[ M_2^{z+} + ze^- \rightarrow M_2 \]

As a result, metal M₂ is deposited in the form of a powder or a continuous film at the surface of active metal. There are many examples of this reaction, Ag/Zn, Au/Ni, Au/Ag, Cu/Zn, Cu/Fe, Cu/Al, Pd/Ni, Pt/Fe, Pt/Co [47].
For autocatalytic deposition: To some less active metals, it is difficult for the metal itself to be deposited. In the autocatalytic deposition there are different kinds of reducing agents including formaldehyde, hydrazine etc.

The existence of the reducing agent can greatly affect the kinetics of electroless deposition, while the surface morphology and physicochemical properties of deposits can be affected as well. Once initiated, this reaction may occur not only at the surface of an object, but in bulk solutions as well, producing powders of various shapes and sizes. In this case the reaction is catalyzed by the metal being deposited [47].

For example, the overall reaction for electroless copper deposition, using formaldehyde (HCHO) as the reducing agent, is

\[
M^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow M^{+2} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2
\]

Electroless deposition, as an indirect-conventional method, has been used for centuries. The biggest advantage of this method is that it does not need to apply an electric current or field through the solution to keep the reaction working; in contrast, a well deposited metal film can be formed on the substrate by electroless deposition under room temperature. Electroless deposition of copper was first discovered by Narcus [50], and ten years later this method was applied and commercialized in industry [51, 52]. Through the years, the detailed formulations have been rapidly developed and updated, resulting in a higher deposition quality, higher deposition rate and highly stable reaction even under a big range of deposition conditions [53-55].

2.2 Materials and Synthesis

2.2.1 Materials

Poly(4-vinylpyridine)(P4VP, Mw ~60,000), silver nitrate(AgNO₃,99%), potassium sodium tartrate tetrahydrate (C₄H₄KNaO₆•4H₂O, 99%), ethylenediaminetetraacetic acid disodium(C₁₀H₁₄N₂O₆Na₂•2H₂O,98%) copper(II) sulfate pentahydrate (CuSO₄•5H₂O,
98%), formaldehyde solution (HCHO, 36.5–38% in H₂O), 2,2-Dipyridyl(98%) are from SIGMA-ALDRICH, 1,4-dioxane(CH₂CH₂OCH₂CH₂O) and sodium hydroxide (NaOH, 97%) both from CALEDON, SU-8(Kayaku Micro Chem). Liquid Tin is from MG Chemicals. All chemicals are used without further purification. The cotton fabric used was from a 100% cotton T-shirt (All-Journey Gear Co. Ltd) bought in Sears without any pretreatment.

2.2.2 Preparation of ELD Solution

The ELD bath solution was prepared in time before ELD process, which contains a mixture of freshly prepared solution A and B. For solution A, 14 g CuSO₄•5H₂O, 16g KNaC₄H₄O₆•4H₂O, 20g EDTA•2Na, 13g NaOH, 20 mg 2, 2-Dipyridyl and 10 mg K₄Fe(CN)₆ are dissolved in 500 mL distilled water in sequence and mixed uniformly to obtain a clear solution. Solution B was 52 mL⁻¹ HCHO in distilled water. The picture of self-prepared solution A and B is shown in Fig. 2-1:

![Figure 2-1 ELD Solution A (left) and B (right).](image)

2.2.3 Synthesis of Copper-coated Cotton Fabric

Surface treatment is needed for deposition of copper. The ratio of P4VP and SU-8 is 10:1.
First of all, 1 g P4VP was first dissolved in 25 ml 2-propanol and 250 µL 40% SU-8 was dissolved in 25 ml dioxane, followed by mixing the two solutions together for 3 minutes using a VWR mixer, shown in Fig. 2-2 until a clear solution was obtained. The cotton fabric sample was dipped in the mixture solution for 3 minutes, dried in air, and then was heated in the oven for 15 minutes at 120 °C for cross-linking. The P4VP-SU8 coated cotton fabric sample was immersed into a 2 g/L silver nitrate solution. The sample was rinsed by distilled water to remove the redundant silver ions after being taken out of the solution. Electroless deposition was performed in each cotton fabric sample for 30, 60, 90, 120, and 150 min, respectively, in an ELD solution, which is used for finding the optimal time for deposition. Fig.2-3 gives a schematic illustration.

**Figure 2-2 VWR mixer.**

### 2.2.4 Characterization

A Hitachi S-4500 field emission scanning electron microscope (SEM) and a Tabletop Microscope TM3030plus were also used to observe the surface morphologies of the textiles. Fourier transform infrared spectra (FTIR) were recorded using FT-IR NICOLET 6700 (Thermo Scientific Co.). The XPS spectra were collected using a Kratos AXIS Ultra XPS from an area approximately 700*300 microns in size, using a monochromatised AlKα X-ray beam. Contact angle was measured by Ramé-Hart Model 100 Contact Angle
Goniometer with micro-syringe attachment (manual system). A four-probe method using an M2750 Keithley Multimeter was carried out to measure the sheet resistance.

Figure 2-3 gives a systematic illustration of the procedures of fabricating copper-coated cotton fabric. Step 1: Pristine cotton fabric and P4VP are connected by polymeric graft chains containing epoxy groups. Step 2: Silver ions are attached to P4VP because of the affinity of pyridyl groups. Step 3: Copper is deposited onto cotton fabric.

2.3 Results and Discussion

2.3.1 The Reason for P4VP-SU8 Chemical Surface Modification

In order to use the method of electroless deposition, strong adhesion between the substrate and metal is needed. The flexible substrate like cotton, plastics cannot seize catalyst moieties well because of a lack of binding sites, and the physical absorption is not stable and often leads to the diffusion of catalyst into the electroless deposition solution. The poor adhesion of deposited metal on the substrate often results in poor
coating quality when the metal layer is too thick, thus it is really imperative to modify the substrate surface before ELD for effective grasp of catalyst moieties and enhanced adhesion of deposited metal to the substrate.

Nowadays, two main methods for surface modification are used, one is surface reforming and the other is surface addition. Surface reforming means to change the surface roughness or preparing active functional groups on the original substrate surface via in situ reaction like oxygen plasma and chemical etching [55,56], while surface addition refers to adding an extra active layer onto the existing surface, including surface silanization [57,58], polymer grafting [59,60] and layer-by-layer deposition of polyelectrolytes [61,62], etc. As said above, two purposes need to be achieved for surface modification, one is to cause the uptake of catalyst moieties selectively and efficiently; the other one is to improve the adhesion.

As a result, surface modification of cotton textiles for ELD should take the two factors into consideration. First of all, modified surface should contain the functional groups that can seize the catalyst moieties effectively; Secondly, the surface after modification should be able to resist plating bath chemically and can operate as a buffer layer between the original substrate and deposited metal for better adhesion. A lot of researches have been done indicating the modified surface can improve the compatibility of metal and substrate, but most methods still cannot satisfy the requirement of scalable low-cost application; some are due to complexity or environment-unfriendly process, and some are because of the difficulty in scaling. For example, substrate modified by the ligand-containing silane cannot resist acid or alkali, so they cannot undergo long-time ELD because of most plating bath contains alkali [61]; the grafting of polymer brush often requires harsh environments and complex steps, and a lot of waste is produced during the process; the speed of layer-by-layer polyelectrolyte deposition is so slow and time-consuming. Conclusively, these methods discussed above are not the best methods for surface of modification of cotton textiles on a large scale.

According to the previous research [63,64], pyridine ligands-bearing poly(4-
vinylpyridine) (P4VP) have been proved as excellent candidates for surface modifier used for grasping transitional metal ions because of its good chelating ability and alcohol solubility. P4VP molecules can be directly coated on the substrate surface [65], but the physical absorption cannot guarantee adhesion of the modified layer. Therefore, enhancing the adhesion of P4VP molecules to the substrates is needed. Previous researches [66] have found out that P4VP has the ability to cross-link epoxy. Based on the analysis above, epoxy is used to cross-link P4VP molecules for two purposes. One aspect is that the reactivity of epoxy is strong so good mechanical and chemical adhesion can be achieved; the other aspect is that a cross-linked polymer network can be obtained because the epoxy molecules can react with each other and P4VP molecules.

2.3.2 Mechanism

In this proposed fabrication method, poly(4-vinylpyridine) (P4VP) and SU-8 are used as the main components of coating solution, and the mixture of 2-propanol and 1,4-dioxane are used as the solvent because of their relatively low boiling point and toxicity. P4VP is first attached to the target textile by dip coating, and subsequently bonds with silver ions. The structure of P4VP is shown in Fig.2-4. P4VP is a very attractive polymer for immobilization of nanoparticles because of the strong affinity of pyridyl groups to metals and its ability to undergo hydrogen bonding with polar species. Cross-linked SU-8 (Fig. 2-5) is well known for its good physical and chemical properties. It can work as a cross-linking agent for P4VP and cotton fabric. When P4VP is mixed with SU-8, pyridine rings of P4VP can start the process of the polymerization of epoxy groups of SU-8 and thus the semi-interpenetrating polymer networks between cross-linked epoxy and P4VP can form. The epoxy groups of SU-8 can also react with hydroxyls groups in cotton, leading to the formation of ether groups. Silver ions absorbed by P4VP have been demonstrated to be an effective seeding and adhesion layer for subsequent ELD of copper to yield conductive textiles in which the metal-deposited textiles show excellent mechanical and electrical properties.
To initiate the copper reduction, palladium or silver ions are needed to serve as the catalyst. Instead of using an expensive PdCl$_2$ activator, we chose a cheaper AgNO$_3$ activator without affecting the properties of the Cu-coating. To immobilize silver ions, surface modification with a functional group is required to provide attractive interaction to ions or nanoparticles. P4VP has been proven to be an excellent surface modifier for immobilization due to the strong affinity of pyridyl groups. The network structured SU-8 is a good cross-linking agent for P4VP and cotton fabric, making P4VP coating more uniform on cotton fabric. The silver ions are first reduced by HCHO, then Ag$^0$ acts as a
catalyst for the subsequent Cu deposition in the electroless coating bath, stimulating copper to act as a self-catalyst in the subsequent reaction. Once the deposition starts, metal will first grow around the catalyst where there are bonds with pyridine ligands, and thus can go deeper into the inside of the modified layer and interlock with P4VP film. As a result, highly adhesive copper layer is formed.

Fourier transform infrared spectroscopy (FT-IR) was conducted to confirm the coating of P4VP and SU8 (Fig. 2-6). In both P4VP/SU8 coated cloth and heat treated P4VP/SU8 coated cloth, the intensity of strong peaks at 1590 cm$^{-1}$, which are attributed to stretching vibrations of pyridone peaks, changed after heating. It was possibly because of ring-opening reaction of epoxy groups of SU8 and the reaction between P4VP and SU8. Moreover, two strong absorption peaks between 1500 and 1600 cm$^{-1}$ which belong to pyridine rings of P4VP molecules don’t change a lot after curing, indicating that only a small amount of pyridine ligands react with epoxide groups due to the content of P4VP outweighs the content of SU-8, so the residual pyridine ligands are still able to uptake the
catalyst moieties.

Table 1 The major elemental analysis of pristine cotton fabric, coated cotton fabric by XPS.

<table>
<thead>
<tr>
<th></th>
<th>C(wt.%)</th>
<th>O(wt%)</th>
<th>N(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton fabric</td>
<td>65.6%</td>
<td>28.9%</td>
<td>0%</td>
</tr>
<tr>
<td>Coated cotton</td>
<td>69.2%</td>
<td>23.7%</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopy (XPS) was also conducted to analyze the surface chemical composition of the pristine cotton and P4VP/SU-8 coated cotton. Fig. 2-7 and Table 1 shows that the carbon content in the sample increased, while the oxygen content decreased after the coating process, during the course of surface treatment. What’s more, the presence of nitrogen was detected after surface treatment, confirming the successful absorption of P4VP. By comparing the C1s spectra of the cotton fabric obtained before and after surface treatment, the intensity of the C-H/C-C peak was found to increase after surface treatment, while the intensities of the O-C-O and C-O peaks are attenuated (see Figure 2-7 XPS spectra of P4VP/SU8 coated cotton.)
Fig. 2-8), because the CH$_2$ and cyclopyridyl contents are increased with the P4VP and SU8 coating.

Figure 2-8 C1s XPS spectra of (left) coated cotton fabric, (right) pristine cotton fabric.

Figure 2-9 Two cotton fabric samples after ELD process; Left: without surface treatment; Right: with surface treatment.

A control experiment was conducted to verify the necessity of surface treatment. One cotton fabric sample was directly immersed into silver nitrate solution without surface treatment, while the other was given the treatment. Both samples were then placed in the copper plating bath for electroless deposition. From the result, in Fig. 2-9, it can be
obviously seen that the left sample (without P4VP/SU8 coating) was almost black while the right one (with P4VP/SU8 coating) had a bright red colour. The colour difference can be attributed to the extent of silver ions absorption. Silver ions were physically absorbed by the sample with no coating, while silver ions were immobilized by the pyridyl groups in the coated sample. Physical absorption tends to absorb more silver ions than chemical absorption because of limited pyridyl groups. During the ELD process, the excessive silver ions absorbed by the sample with no coating were easily reduced to silver, but they tend to diffuse into the solution and hardly play as a stable catalytic center for immobilization of subsequent fresh copper atoms. The inconsistent layer of nano-sized silver particles resulted in the poor conductivity of the sample without coating.

2.3.3 Find the Best Concentration and ELD Time

To find the best P4VP concentration, four solutions with different P4VP concentration ranging from 1% to 4% were prepared. The ELD time was set to 90 minutes. The sheet resistance was measured using Keitheley 2750, as shown in Fig. 2-11. The sample was put on the platform of the four-probe meter to be touched by the four probes simultaneously. For each sample, five measurements were conducted on the different points of the sample. The median and deviation were calculated based on the five results. The conductivity of the cotton fabric sample in the 1% concentration was poor compared to the other samples. This was because less P4VP means fewer amino groups, where fewer Ag\(^+\) moieties were immobilized, thus affecting copper plating. The conductivity of cotton fabric samples in 2%, 3% and 4% concentration were close and didn’t vary too much from 2% to 4%. However, from outward appearances, the copper was distributed uniformly on the 2% sample and there were some copper clusters formed on the 3% and 4% surface. The higher the P4VP concentration is, the greater the viscosity of the solution is, and the poorer the fluidity is. The poor fluidity of P4VP solution may result in the nonuniform coating on the cotton fabric surface. The formation of copper clusters may be due to the fact that the catalytic speed is higher in the place with more P4VP molecules loaded. Conclusively, we adopted the 2% concentration as the optimal choice.
The weight gained during the ELD process should have been proportional to ELD time. It was observed that the weight increased as a linear function of ELD time (Fig. 2-12). The weight reached 106% of its original weight after 150 min. It can be seen that the copper layer accumulated quickly and continuously within the first 2 hours. During the first hour, the copper layer growth rate was higher due to high initial concentration of copper ions. With the reaction going on, the consumption of copper ions and hydroxide ions make the
The growth rate is slow down.

**Figure 2-12** Weight gain after ELD at different ELD plating time.

**Figure 2-13** Sheet resistance of copper cotton at different ELD plating time.
Figure 2-14 From left to right, color of each cotton fabric sample at different ELD plating time 30, 60, 90, 120 and 150 min.

The sheet resistance of the copper cotton sample was also studied, which is a measure of resistance of thin films. Sheet resistance is a strong function of thickness. To reduce error, we measured several points on the both sides of the copper cotton sample and calculated the average as the final result. We demonstrated the effect of time on sheet resistance when ELD plating time varied from 30 min, 60 min, 90 min, 120 min and 150 min. The average sheet resistance of the sample was plotted against ELD plating time, as shown in Fig. 2-13. Fig. 2-14 shows the color of cotton fabric sample at different ELD time. The pristine cotton sample and P4VP-SU8 coated sample were electrically insulated. After 30 minutes of ELD, the sample became electrically conductive, but its resistance was as high as 0.25 $\Omega \text{sq}^{-1}$. Most of the surface appearance of the sample still remained black, which can be explained by the color of silver particles. The silver particles did not catalyze the reduction of copper ions fully enough and were still absorbed on the surface. After 60 minutes, it could be seen that the black areas decreased dramatically and the sheet resistance decreased a lot to 0.15 $\Omega \text{sq}^{-1}$. When the ELD time was extended to 90 minutes, black areas almost diminished and the color of the copper cotton sample turned to a red copper color. The sheet resistance decreased to 0.05 $\Omega \text{sq}^{-1}$. When the ELD time was
extended to 120 minutes, the sheet resistance decreased to 0.04 Ωsq\(^{-1}\) and remained almost the same even for the deposition longer than 120 minutes, which was consistent with the weight gain. Considering all factors including efficiency and conductivity, 90~120 minutes of the ELD is an appropriate time for copper deposition. According to the equation \(\rho = R_s t\), where \(\rho\) is the bulk resistivity, \(t\) is the thickness, \(R_s\) is the sheet resistance. We can approximately calculate the bulk resistivity of as-deposited copper \(\rho\) after two hours, which is approximately 3 times of normal bulk copper. Low resistance will apparently decrease the waste of electrical energy and make it a perfect conductor in flexible electronics.

2.3.4 Morphology

Although the surface morphologies of P4VP-SU8 coated cotton and untreated cotton look quite similar, water contact angle measurement shows their gigantic difference in surface wettability. Cotton is a hydrophilic natural polymeric material. When a droplet of water was dropped on the surface, it quickly soaked into the fabric and disappeared. After the P4VP-SU8 coating, the cotton fabric surface became quite hydrophobic because P4VP is water insoluble and SU-8 is hydrophobic. The water contact angle was 110.5° (Fig. 2-15 B). After the ELD process, the surface of the cotton fabric sample was covered with a layer of uniformly distributed and densely packed copper particles (Fig. 2-16), which was further proved by energy-dispersive X-ray spectroscopy (EDS) (see Fig. 2-17). The EDS analysis also showed that 80% was copper, which showed that the copper film formed during the ELD process surrounded every fiber uniformly. After copper deposition, the surface became hydrophobic again and the contact angle was 95.8° (Fig. 2-15 C).
Figure 2-15 SEM images of (A,A’) pristine cotton fabric; (B,B’) P4VP/SU8 coated cotton fabric;(C,C’) copper cotton fabric.

Figure 2-16 Enlarged SEM image of copper nanoparticles coated on cotton textiles.
When we pulled a single yarn from the cotton fabric sample, it can be seen that some parts of the yarn were not fully covered with copper (Fig. 2-18). It is proposed that the up-and-down inter-crossed structure of the warp and weft yarns and the twisting of cotton fibers prohibit the exposure to P4VP. Surfaces exposed to P4VP/SU8 solution are merely allowed the crosslinking reaction, so as the subsequent occurrence of ELD of copper metal particles. As a result, a single yarn pulled from the cotton fabric sample has a much higher resistance. We also studied the silver ions distribution at the intersection of cotton fabric sample before ELD process. From the EDS analysis result, it can be seen that there are little silver ions found. The silver ions mainly exist on the surface of cotton fabric (Table 2). From this, it can be inferred that the conductivity of the copper-coated fabric mainly relies on the closely packed woven structure that makes copper metal particles tight together closely. As long as the woven structure is compact, the conductivity of cotton fabric won’t be much affected.
Figure 2-18  Examination of single yarn pulled from copper-coated fabric sample.

Table 2  The major element analysis at the intersection of cotton fabric sample after absorbing silver ions.

<table>
<thead>
<tr>
<th></th>
<th>C(wt.%)</th>
<th>O(wt.%)</th>
<th>Ag(wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton fabric before</td>
<td>3.74%</td>
<td>43.73%</td>
<td>52.53%</td>
</tr>
<tr>
<td>ELD</td>
<td></td>
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2.3.5 Mechanical Test

2.3.5.1 Stability Test

The conductivity change of the copper cotton sample under aging was evaluated and the sheet resistance of copper cotton (2% P4VP and 90 min ELD) was recorded when it was stored in air for a certain amount of time. It was discovered that the sheet resistance increased to 158% after one day and then remained almost unchanged for the rest of the next two week proving the long-term stability, as shown in Fig. 2-19. According to the previous study [69], the increase in resistance was due to the partial oxidation of Cu into Cu$_2$O. Therefore, for application purposes, a passivation layer should be deposited over the nanowire coating to prevent degradation over time. A layer of air-stable metals, such as tin, can be capped on top of copper. Liquid Tin is a clear immersion tin designed and formulated to coat a copper substrate with a dense tin deposit. The tin deposit owes its outstanding corrosion protection to its dense coating. After ELD process, the fabric sample was dipped into the liquid tin solution for one hour, and a layer of tin was formed.

Figure 2-19 Resistance aging test of the copper cotton sample.
because of replacement reaction (Fig. 2-20). The sheet resistance of the as-made Sn-Cu cotton fabric was, however, a little bit lower than the Cu cotton.

Figure 2-20 Sn-Cu cotton fabric sample.

2.3.5.2 Bending Test

To apply the conductive cotton in real world, it must be mechanically flexible and keeping the resistance from degrading significantly after repeated bending cycles, especially when used in daily applications like sensors integrated in clothing. Copper thin films are brittle and easy to crack after repeated cycles, and the resistance increases after the cycles [69]. Films of copper nanoparticles, on the other hand, are more flexible. The nanosized diameters of copper nanoparticles and geometry are known to make them more flexible and stringer than the bulk-like counterparts, so they can withstand higher elastic strain [70]. The bending radius is 30 mm for the bending cycle test. It can be seen from Fig. 2-21, the resistance doesn’t change much after bending 100 cycles, the resistance only increases very little, proving the stability of this method.
Figure 2-21 Resistance change test at different bending cycles.

Figure 2-22 Resistance change test of the copper cotton sample at different bending radius.
The relationship between the electrical resistance and different radii of curvature was investigated (Fig. 2-22). To make the measurement more precise, different cylinders with different diameters ranging from 1mm to 30 mm were printed using 3D printer. The sample was bent with the help of 3D-printed cylinder to help control the bending radius. The electrical resistance decreased as the bending radius decreased, which was the same as what Zheng’s group found [69]. They pointed out that when the copper cotton sample is bent to a small radius, the sample is subject to higher tensile strain, enabling the cotton fibers and yarns to be stretched to form a more compact contact between each other, improving the connections between overlapping nanoparticles while lowering junction resistance and decreasing the contact resistance.

2.3.5.3 Washing Test

The adhesion of copper coating is also crucial to conductive textiles. A washing test was conducted to evaluate the adhesion of the copper coating to cotton fabric. At first, some detergent was put into a tube full of distilled water, and then the conductive cotton fabric was immersed in the tube and shaken for 5 minutes, and waited for the cotton fabric to dry for subsequent measuring of resistance. The whole steps were repeated for 5 times. The resistance kept the same shown in Fig. 2-23, which pointed out that the coating did not come fall off or degrade and the chemical pretreatment of the cotton fabrics provides excellent adhesion.
Apart from efficiency and convenience, as mentioned above, the surface treatment did not affect the flexibility and leave traces. Thus, another great advantage of this method is that it can print different kinds of functional patterns on cotton textiles using a normal home use printer. Many approaches have been proposed for the fabrication of metal patterns on rigid or flexible substrates, like photolithography [71], inkjet printing [72], contact printing [73], screen printing [74], direct pen writing [75] and so on. But few approaches have been proposed for fabrication of metal patterns on cotton textiles. Instead of the whole cotton cloth being immersed in silver nitrate solution, patterns can be directly printed using a printer with silver ink inside after surface treatment. The silver ink used here was composed of silver nitrate, distilled water and glycerol. By printing a layer of catalyst, copper can only grow on the area of exposed catalyst. First of all, the cotton cloth was pretreated with P4VP/SU8; Secondly, the cotton cloth was attached onto

Figure 2-23 The resistance of copper coated sample after washing.

2.3.6 Ink-jet Printing Patterns on Cotton Textiles

Apart from efficiency and convenience, as mentioned above, the surface treatment did not affect the flexibility and leave traces. Thus, another great advantage of this method is that it can print different kinds of functional patterns on cotton textiles using a normal home use printer. Many approaches have been proposed for the fabrication of metal patterns on rigid or flexible substrates, like photolithography [71], inkjet printing [72], contact printing [73], screen printing [74], direct pen writing [75] and so on. But few approaches have been proposed for fabrication of metal patterns on cotton textiles. Instead of the whole cotton cloth being immersed in silver nitrate solution, patterns can be directly printed using a printer with silver ink inside after surface treatment. The silver ink used here was composed of silver nitrate, distilled water and glycerol. By printing a layer of catalyst, copper can only grow on the area of exposed catalyst. First of all, the cotton cloth was pretreated with P4VP/SU8; Secondly, the cotton cloth was attached onto
a paper for printing silver ink; Finally, ELD was performed on the cloth for deposition of copper. Fig. 2-24 shows the detailed schematic diagram for the production of copper patterns by employing printer to print catalyst on the modified substrates. The inkjet printing method provides benefits like speed, flexibility, non-contact and creativity. Basically, just a print head and ink are needed to print whatever you want, like antennas, circuits and other patterns. As Fig.2-25 shows, Western University’s logo was printed on a piece of cotton cloth. Importantly, the whole process is carried out in air and aqueous environments, which are more compatible with typical roll-to-roll fabrication processes in the textile industry. More importantly, this method can be extended to apply on PET and 3D printed object, shown in Fig. 2-26, Fig. 2-27, showing the universal applications of this technique.

Figure 2-24 Schematic diagram for the production of copper patterns by employing printer to print catalyst on the modified substrates.
Figure 2-25 Western University’s logo printed on cotton fabric.

Figure 2-26 Digital photos of some typical flexible printed circuits obtained by printing toner mask followed by electroless copper deposition on PET film. (Copy from [76] )
Figure 2-27 As-proposed ELD method was applied on 3D objects for surface metallization of 3D structure.
Chapter 3

3 Applications of Conductive Cotton Textiles

3.1 Flexible Pressure Sensor

3.1.1 Introduction of TPU

Polyurethane is one kind of polymer which consists of a chain of organic units linked by urethane linkage (-NCOO-). Thermoplastic polyurethane (TPU, Fig. 3-1) is a unique category of plastic created when a polyaddition reaction occurs between a diisocyanate and one or more diols. First discovered in 1937, this polymer is soft and processable when heated; returns to hard state when cooled and capable of being reprocessed multiple times without losing structural integrity [77]. Polyurethane has increased really quickly to be one of the most widely used polymer and been continuously increasing market share since its discovery in 1937 [78]. According to a report online in 2010, 13650 kilo tons of polyurethane were in need. It is expected to increase to 18000 kilo tons in 2016 with an annual increasing rate of 4.7% and the market value is expected to be 55480 million USD [79].

Used either as a shapable engineering plastic or as a replacement for hard rubber, TPU is famous for many features: resistant to action of microorganisms; increased hardness by adding filler such as glass fiber; good resistance to hydrolysis; high elongation and tensile strength; elasticity; the ability to resist oil, grease, solvents, chemicals and abrasion to varying degrees; flexibility [77]. These properties make TPU extremely powerful across a range of applications and markets, shown in Fig. 3-2. Because of its inherent flexibility, it can be molded on the traditional thermoplastic manufacturing machine to form daily products like footwear or other industry products. Compared with some traditional materials like metals and wood, polyurethane has many advantages over them, because of the advantages mentioned above like low density, low thermal conductivity and high dimensional stability. That’s the reason why polyurethane is in such great need [79].
3.1.2 Introduction of Conductive Polymer

Polymers have been considered to be excellent candidate materials for electrical insulators in electronic and electrical fields. The resistivity of most polymers is very high, generally around $10^{15}$ ohm$\cdot$m. However, to utilize the properties of these polymers, some material designers have begun to think about imparting conduction to polymers by
mixing the insulating polymers with some conductive materials like carbon, metal particles or some conducting polymers like polyaniline [82]. As a result, a variety of so-called conductive polymer composites has come to existence since 1950s [83] with the resistivity between the metal conductors and insulators. These as-made conductive polymer composites can find their applications in a lot of fields like electronics equipment [84, 85], electromagnetic interference shielding [86]. Nowadays, these conductive composites have been used for sensing elements [87, 88]. Because compared with other conductors, conductive polymers composites have the merits of low density, ease of deforming and shaping, and a wide range of electrical conductivities.

Nowadays, carbon fibers and carbon black particles are commonly used conductive components to increase conduction to polymer composite. The reason is because carbon black particles are much easier to form a conductive network because of their chainlike aggregate structures when compared to other conducting materials like metal powder, whilst carbon fibers are considered as chain-like aggregates of carbon particles with long chain length [89].

Conductive polymer composites (CPC) have attracted attention because of their quick response in electrical resistance when subjected to pressure. There are two ways to obtain conductive polymers: produce a polymer that is intrinsically conductive or mix the polymer matrix with conductive fillers. To make conductive polymer, it is necessary to disperse one or more electrically conductive fillers in the insulating polymeric matrix. A number of conductive materials have been used to fabricate CPC, like carbon nanotube, graphene, carbon black [89].

3.1.3 Preparation of Carbon Black /TPU Electrode

3.1.3.1 Materials and Chemicals

Carbon black (Cabot Corporation), Polyester-based thermoplastic polyurethane (TPU) (Elastollan 1185A) with a density of 1.12 g cm$^{-3}$ (215 1C, 10 kg) was obtained from BASF Co. Ltd. It was dried at 80 °C under vacuum for 12h before usage. Dimethylformamide (DMF) is supplied by Sigma-Aldrich. All of the organic solvents
were used as received without any further treatment.

3.1.3.2 Fabrication

Briefly, 2.0 g of TPU was dissolved in 35 mL of DMF at 40 °C by vigorous stirring for 15 min. The required amount of carbon black was mixed with 15 mL of DMF and treated under ultrasonication for 10 min to disperse the carbon black homogenously. Subsequently, the TPU/DMF and carbon black/DMF were mixed together and stirred vigorously on a hotplate of 60 °C for an additional 60 min. Then the whole mixture was cast into a metal petri dish homogeneously, then dried on an 80 °C hotplate for evaporating the DMF. The thickness of the nanocomposite was about 0.5 mm. The as-made TPU electrode is shown in Fig. 3-4.

![Diagram of the process for the fabrication of carbon black/TPU composites.]

Figure 3-3 Illustration of the process for the fabrication of carbon black/TPU composites.
Generally, the introduction of conductive fillers into the insulating polymers will provide the resulting composites with good electrical conductivity. The volume resistance was measured using a Keithley 2400. The volume resistance of TPU as function of carbon black content is depicted in Fig. 3-5. It can be clearly seen that the resistance decreases as the content of carbon black increases. The decrease in resistance is due to the formation of the conductive network in the TPU matrix. The bulk resistance is about 70k ohm. We choose 1% as the CB content because even higher carbon black content has lower resistivity, the mechanical properties might be affected.
3.1.4 Why Choose TPU as Electrodes

There are many considerations for choosing electrodes for flexible pressure sensors. In fact, electrodes can be part of sensitive elements in pressure sensors. Especially, in piezoresistive sensors, the applied pressure stimulates a resistance change due to the contact change between two electrode sheets, generating a signal output. For the exploration of conductive electrodes, stability and mechanical flexibility should be taken into account to achieve the goal of flexibility. A lot of groups have chosen carbon and elastic composites for use over the currently used metal electrodes, like gold, silver and copper. The advantage using conductive elastic composite other than normal metal electrode is that it can withstand more strain and the resistance of itself changes with the pressure. For instance, carbon nanotubes and graphene are excellent electrode materials because of their mechanical flexibility and high conductivity [90]. Compared to PDMS, carbon materials are easier to be dissolved in polyurethane solution and the fabrication processes are more convenient [91].

Figure 3-5 Resistivity vs. carbon black content of TPU.

![Figure 3-5 Resistivity vs. carbon black content of TPU.](image)
3.1.5 Assembly of the Pressure Sensor

Fluffy cotton sheets were given electroless deposition for better sensitivity, shown in Fig. 3-6. This flexible pressure sensor was assembled using two pieces of as-prepared conductive TPU sheets with face-to-face orientation, shown in Fig. 3-7. The TPU electrodes were stacked on the terminals of conductive fluffy cotton sheets using silver paste and after that the flexible pressure sensors were bonded together using copper tapes at two edges.

![Figure 3-6](image_url) Untreated fluffy cotton (left), copper coated cotton (right).

![Figure 3-7](image_url) Structure of the flexible pressure sensor.
3.1.6 Performance of this Flexible Pressure Sensor

The resistance of the pressure sensor changes when an applied force induces a structure change in the contact area of copper coated cotton fibers at the surface of the bottom and top cotton sheets. The response of this flexible pressure sensor is shown in Fig. 3-8. Electrical measurements were performed on a Keithley 2400 sourcemeter. As you can see from the graph, it is observed that there is a big decrease in resistance when the pressure applied on the sensor. Fig. 3-8 demonstrates the response to an immediate applied pressure and the relaxation properties of this flexible pressure sensor, showing that the sensor’s structure greatly influences the relaxation and response time. The relaxation and response time is about 45 ms. Fig. 3-9 demonstrates that the resistance signal change generated by sensing an object on and off are reversible and continuous.

As shown in Fig. 3-10, the cotton fibers at the cross point is compressed under the external applied force because of the viscoelasticity. The piezoresistance is largely influenced by the contact resistance at the sensor film, which is largely dependent on the contact area resistance. In this device, the contact area where the interconnected cotton fibers cross changes more easily under the applied force because of the viscoelasticity of cotton fibers and the relatively unstable transmission path of the current. That’s why a rapid response is achieved for the flexible pressure sensor. Besides, good elasticity and flexibility of TPU and cotton textiles are the reasons behind a good response.
Figure 3-8 Response time for the flexible pressure sensor.

Figure 3-9 Pressure-dependent resistance recorded by putting an object on and off.
Pressure was applied or released by adding or reducing different weights onto the device, shown in Fig.3-11. The weights from the balance consist of 1 g, 2 g, 5 g, 10 g, 20 g, 50 g, 100 g, 200 g. The pressure was calculated by the ratio of the weights used and the cross-section area. Each resistance was written down after a weight was put on the pressure sensor. The sensitivity of the pressure sensor using copper-coated cotton sheet is around 1.5 kPa⁻¹, shown in Fig. 3-12.

Figure 3-10 Schematic illustration to demonstrate the structure change at the junction under the external force.

Figure 3-11 A weight was put on the pressure sensor.
To prove the stability of the as-made pressure sensor, a stability test was conducted. Fig. 3-13 demonstrates the compression repeatability of this flexible pressure sensor, showing that the sensitivity can maintain after 100 loading cycles and proving the good working stability of our flexible pressure sensor.

Figure 3-12 The resistance change under different pressures.
Figure 3-13 Sensitivity of pressure sensors under different loading cycles.

Under the external force, the cotton fibers contact each other more closely due to the viscoelasticity, which leads to the immediate response of the pressure sensor. According to the paper [92, 93], for the cross point, the junction resistance \( r_{\text{total}} \) can be estimated using the following equation:

\[ r_{\text{total}} = r_{\text{bulk}} + r_{\text{in}} \]

where \( r_{\text{bulk}} \) represents the bulk resistance, \( r_{\text{in}} \) represents the resistance at the interface between two cotton fibers. After an external force is applied at the interface, the resistance change at the crosspoint can be estimated as:

\[ \Delta r = r_{\text{in}} - r_{\text{in}}' \]

where \( r_{\text{in}}' \) is the resistance at the junction after a force is applied on the cross point, thus the resistance change of this pressure sensor can be expressed in the following equation:
\[ \Delta R = R_{in} - R_{in}' \]

In the equation above, \( R_{in} \) represents the whole interface resistance of the pressure sensor, while \( R_{in}' \) means the whole interface resistance after an applied force.

The flexible pressure sensor is very sensitive and can detect the gentle pressure. What’s more, the pressure sensor has the potential applications for wearable human motion detection because of the high sensitivity and repeatability. When the sensor is put on a volunteer’s middle finger, at first the middle finger is naturally kept straight and the pressure sensor is in an original shape where there is no outside pressure. Once you bend your middle finger, there will be a pressure applied to the pressure sensor, resulting in an immediate decrease in resistance. After the middle finger moves back to its original state, the stress decreases and the sensor relaxes, as a result, the sensor returns to its original shape and the resistance changes back to normal, as shown in Fig. 3-14. The sensor is also mounted onto the volunteer’s opisthenar to monitor the hand motion. When the volunteer makes a fist, it is observed that there is an immediate decrease in resistance; and the resistance changes back to normal after the hand is straight again, shown in Fig. 3-15. The effectively continuous monitoring of human body motion makes this flexible pressure sensor a perfect sensor that can be used in robotics and wearable electronics.
Figure 3-14 Demonstration of motion detection of the middle finger.

Figure 3-15 Demonstration of motion detection of the opisthenar.
In conclusion, the whole processing method is very convenient, simple, non-toxic and biodegradable, and have the ability to be fabricated on a large scale.

3.2 Textile Electrode for ECG Monitoring

3.2.1 Structure of the Textile Electrode

After fabricating the conductive cotton textiles, the copper-coated textile is used to make a skin electrode which can obtain bio-signal recordings from human body. The structure of the whole electrode is shown in Fig. 3-16. A metal snap is used to connect the textile electrode with the protective strap. Thus, the whole ECG sensor can be wrapped around forearm with this strap, making it convenient for measuring ECG signals.

![Figure 3-16 Structure of this textile ECG electrode.](image)

3.2.2 Performance of the Textile Electrode

A commercial data acquisition system (NeuroSky Inc.) provides a convenient means to record ECG signals detected with this textile electrode. This experiment setup consists of a USB-type receiver and a laptop computer with customized data recording software.

The volunteer sat still for 30 minutes and relaxed himself before measuring ECG signal.
During the ECG recording, two textile electrodes and two Ag/AgCl electrodes are fixed to the volunteer’s left and right arm as shown in the Fig. 3-17. A wire with snap is used to connect the electrode with the receiver. Customized software is used with an interface shown in Fig. 3-18.

![Textile electrode on the forearm for ECG measuring.](image)

Figure 3-17 Textile electrode on the forearm for ECG measuring.
To prove the effectiveness of this new dry electrode, we measured the ECG signals using this textile dry electrodes and Ag/AgCl electrodes, and the results are shown in Fig. 3-19.

In comparison with the result of the dry and the Ag/AgCl electrodes, there are no obvious observable differences between these two signals. The time interval and the values of high peak and low peak are the same. All the P, QRS, and T waves can be detected clearly. The signal waveform from the dry electrode is almost similar to that from the Ag/AgCl electrode.

Figure 3-18 The data recording software interface.
3.2.3 Electrical Characterization

Figure 3-19 Comparison of ECG signal performance (upper) textile electrode and (down) Ag/AgCl electrode.

Figure 3-20 Equivalent circuitries of the dry skin-electrode interface. (Copy from [94])

For the dry electrodes, due to the lack of the conductive gel, the coupling between the
skin and the electrode is capacitive. The dry electrodes, especially the rigid or hard electrode, cannot completely conform to the skin, resulting in gaps or air in between, which functions as a dielectric layer. The sweat on the skin surface increases the resistance between the skin and electrode. Therefore, the skin-electrode interface can be modeled by a parallel connected resistor $R_g$ and capacitor $C_g$, shown Fig. 3-20. Since human sweat has a similar but less effective function to the electrolyte, $E_{hc}$, a half-cell potential is used to describe the interface with the interface with the electrode. Normally, the skin-electrode impedance for the dry electrode is larger than that of wet electrode because of the poor contact with the skin. The impedance largely relies on the external pressure and skin humidity. External pressure can improve the contact and thus decreases contact impedance [95]. As said before, the hydration caused by sweat can reduce the overall skin impedance by enhancing the conductivity [96, 97]. Normally, the skin-electrode impedance will decrease after applying the dry electrode for some time. So the motion artifacts of the dry electrode are initially high but it decreases even to the level that can be compared to wet electrode after some time. If the dry electrode is made of stiff or rigid materials, then it is hard to conform to the skin, which may result in higher impedance and higher motion artifacts. So flexible surface electrodes are much better compared to rigid dry electrode, because it can better adapt to different curve or shape, thus achieving a more stable and comfortable interface.

Then skin electrode impedance was characterized by LCR Meter (E4980A) frequency from 0.1 kHz to 3 kHz over the skin-mounted electrodes, which were placed 5 cm apart on the inner side of the forearm, as reported in [98].

Fig. 3-21 illustrates the average impedance values in the frequency range of 0.1 kHz to 3 kHz. The impedance decreases as the frequency increases. The impedance of the copper coated textile ranges from 1000k Ohm to 50k Ohm, which is a little bit higher than conventional electrodes [99], but it is still within the range of impedance values for dry textile electrode which are as large as several hundred kilo ohms to mega ohms [100,101].
In Fig. 3-21 also shows the pressure influences the electrode-skin impedance. As expected, the skin-electrode impedance decreases with pressure, which is mainly attributed to the increased contact area. But in the high frequency range, the pressure does not have a strong effect on reducing the impedance.

Figure 3-21 Electrode-skin impedance with increasing application pressure.
Chapter 4

4 Thesis Summary and Future Direction

4.1 Thesis Summary

Stretchable and flexible electronics that can measure or quantify electrical signals of humans are receiving more and more attention because of these new and unique characteristics like light weight, high flexibility, ultra-thinness and stretchability. Electronic textiles are part of stretchable and flexible electronics, which are currently used in the fabrication of antennas, pressure sensors, supercapacitors, batteries, electromagnetic interference (EMI) shielding devices and electrophysiological sensors. They have been considered as important applications for next-generation wearable electronics and smart clothes, which combines the multi-functionality of electronics devices as well as the comfort and warmth of clothes. The thesis mainly focuses on a facile way of fabricating conductive cotton textiles via electroless deposition. Two sensors were fabricated based on the conductive cotton textiles.

Chapter 1 introduces the necessity and importance of developing e-textiles. Different coating methods and coating materials are introduced. The basic cardiac physiology principle is introduced and two types of ECG sensors are compared. Different types of pressure sensors are also mentioned and the mechanisms of three types of pressure sensors are explained.

Chapter 2 gives the detailed fabrication method of conductive copper-coated cotton. The reason why we use P4VP and SU8 for surface treatment is discussed. The best ELD parameters are discovered. Characterization of the as-made copper-coated textiles is analyzed. Mechanical and electrical tests are also performed, demonstrating this technique is promising for future applications.

Chapter 3 is divided into two parts. The first part is preparation of conductive TPU electrode and assembly of this pressure sensor. The response time and repeatability shows
satisfactory results. This pressure sensor can clearly detect muscle motion for potential applications in motion control. The second part is using the conductive textiles as dry electrodes for ECG measurement. The signals obtained from this textile electrode are as good as conventional Ag/AgCl electrodes.

4.2 Limitations and Future Direction

We only measured the resistance change after two weeks. The long-term stability like more than one year cannot be guaranteed. It is likely the resistance of the copper nanoparticles may change after one year under moist conditions. The linearity of the pressure sensor is only under 300 Pa, so it is not suitable for quantitative measurement of the specific pressure.

The fabrication procedures have been explored for conductive textiles via electroless deposition. We can extend this application beyond copper, nickel and gold can also be explored. More substrates can be tested to prove this technique universal for different substrates.

For the flexible pressure sensor, sensors with microstructures could demonstrate better performance relative to their unstructured counterparts, owing to their anisotropic structure. We can use etched silicon wafer as substrate and cast the TPU on the silicon wafer to fabricate structured electrode to increase the sensitivity. For the textile electrode, we can deposit a layer of tin to make the electrode friendlier for human skin.

More applications can also be explored for the conductive cotton textiles, like electrodes in supercapacitors, electrodes in solar cells, patterned RFID tags.
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Curriculum Vitae

Name: Sicong Liu

Post-secondary
Northwestern Polytechnical University

Education and
Xian, Shaanxi Province, China

Degrees:
2010-2014 Bachelor of Engineering Science

The University of Western Ontario

London, Ontario, Canada

2014-2016 Master of Engineering Science

Honours and
First Class Scholarship

Awards:

Related Work
Research/Teaching Assistant

Experience
The University of Western Ontario

2014-2016

Publication: