SILVER NANOWIRE INKS FOR FABRICS

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Conductive inks are used extensively in electronic devices like sensors, batteries, photovoltaic devices, antenna and organic light emitting diodes. These inks typically made from silver. Wearable technology is another industry which requires inks to be flexible. These devices need low temperature cured silver pastes. Low temperature pastes typically make use of silver nanoparticles. These pastes have some problems with sintering and substrate adhesion. In this thesis, to overcome these problems, silver nanowires are used to formulate pastes. Conductivity, bonding strength, flexibility, transparency and compliance of the silver nanowire pastes were determined. Promising performance of was obtained from silver nanowire pastes due to the one dimensional nature of the nanowires in terms of adhesion to fabric surface. Silver nanowires have a big area to adhere, network form of them is more conductive and transparent than network form of silver nanoparticles. The aim of this study is fabrication of low temperature silver paste by synthesis long silver nanowires.
Keywords: silver nanowire, silver ink, low temperature conductive ink
ÖZ

KUMAŞ İÇİN GÜMÜŞ NANOTEL MÜREKKEPLERİ

Güven, Merve Nur
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Anahtar Kelimeler: gümüş nanotel, gümüş mürekkep, düşük sıcaklıkta kürlenebilen gümüş mürekkep
To My Precious Family and My Lovely Husband
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## Abbreviations

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<th>Full Form</th>
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<tbody>
<tr>
<td>1D</td>
<td>One Dimensional</td>
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<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>Silver Nitrate</td>
</tr>
<tr>
<td>Ag NWs</td>
<td>Silver Nanowires</td>
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<tr>
<td>Au</td>
<td>Gold</td>
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<tr>
<td>CMC</td>
<td>Carboxy Methyl Cellulose</td>
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<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>Copper Chloride</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
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<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
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<tr>
<td>EtOH</td>
<td>Ethanol</td>
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<tr>
<td>LCD</td>
<td>Liquid Crystal Display</td>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>NaBH₄</td>
<td>Sodium Borohydride</td>
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<td>NaCl</td>
<td>Sodium Chloride</td>
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<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>NMP</td>
<td>N- methyl Pyrrolidone</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowires</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
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<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silicon Dioxide</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium Oxide</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet Visible</td>
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SYMBOLS

\( \Omega \)  Ohm

\( ^\circ \)  Centigrate

\( \mu \)  Mikro
CHAPTER 1

INTRODUCTION

1.1. Nanotechnology and Nanomaterials

Metallic one dimensional (1D) nanostructures have unique optical, electrical, catalytic and thermal characteristics. Due to these valuable properties, they gain a valuable role and received significant attention in electronic devices. Three parts are essential for conductive inks which are conductive fillers, solvent and binder. Micron sized metal powders or flakes are typically used as conductive fillers and silver nanowire inks. Silver nanowires can be used as fillers in conductive inks, which has not been explored in detail. This is highly promising since silver nanowires can be sintered or heated at low temperatures following printing to make printed pattern more conducting. Therefore, silver nanowire based inks are highly promising for wearable electronics where the thermal budget is very low.

While synthesis nano scales particles by micro scale ones, some physical and chemical properties are changed because of high surface energy. Nano rods, nano tubes, nano particles and nanowires are typically types of metallic one dimensional nanostructures which are useful for transparent conductive materials [1].

Nanotechnology refers to efforts synthesis materials with dimension between at least in 1 and 100 nm. Thanks to nanotechnology, weight and power consumption of electronic devices decrease while the device capabilities increase. Nanotechnology offers many advantages for electronic devices such as;

- Size of integrated circuits transistors is decreased.
- Screens of electronic devices are developed.
- Density of memory chips is enhanced[2].
Scientists have great concern to nanotubes, nanorods, nanoribbons and nanowires because of interesting size dependent and structure related properties resulting from confinement effects and also their unique catalytic, thermal, optical and electronic properties.

1.2. Nanowires

Nanowires have one dimensional on large scale and their dimensions are approximately between 1-100 nm. Their two dimension refers to their nanoscale while one dimension refers to their electrically and optically properties. As can be understood from their dimensions, their configuration is specific and it gives high qualities in terms of electrical, thermal, magnetic and optical. They have also known as quantum wires thanks to their unique quantum mechanical properties[3].

Nanowires have many advantages to use in electronic devices in terms of power consumption and tiny size.

There are four various types of nanowires which are insulating nanowires, molecular nanowires, semiconducting nanowires and metallic nanowires. Metallic nanowires are usually made up from nickel (Ni), gold (Au) or platinum (Pt). If nanowires are made from titanium dioxide (TiO$_2$) or silicon dioxide (SiO$_2$), they are called as insulating nanowires. A nanowire includes repeating inorganic or organic molecules, it is called as molecular nanowires while a nanowire includes gallium nitrate, silicon or indium phosphide, it is known as semiconducting nanowires[4].

1.2.1. Properties of Nanowires

There are four kinds of important properties for nanowires which are optical properties, mechanical, magnetic and catalytic properties. All important information about each is given below.

The first important characteristics of nanowires is catalytic properties. Transition metal oxide nanowires have a large surface to volume ratio; that is why, they
demonstrate catalytic properties of these oxides[1]. If these nanowires are coated or combined with platinum or gold, their catalytic properties are improved[1,2,5].

The other property is optical property. Non agglomerated nanowires can be used as refraction hence a material with non-linear optical properties or visual properties could be produced. With decreasing size of silver nanowires, fluorescence performance of some oxide polymer nano composite shifts to blue while gold and lead nanoparticles cause to orange or red shifting semiconducting nanomaterials in glass [2].

Mechanical property is another important property of nanowires. If a bulk is nanowire based and it has huge grain boundaries, these boundaries provides to high flexibility.

The last property of nanowires is magnetic properties. Super magnetism is the reason of fluctuation of magnetization vector because of magnetic anisotropy. Super magnetic materials are coercitivity and reminiscence free. These properties are lost by touching these particles to keep them at distance. A new permanent magnetic materials could be created by combination of a super magnetic material and an anisotropy material with high energy[2].

1.3. Silver Nanowires

1.3.1. Synthesis of Silver Nanowires

There are so many procedures to synthesize silver nanowires. In the beginning of history of silver nanowire synthesis, electrochemical method was used; however, yield of synthesized silver nanowires was so low and they were not uniform. After synthesized not uniform silver nanowires, hard and soft template methods were started to be used instead of as an electrochemical methods[6].

1.3.1.1. Hard Template Methods

Synthesized of silver nanowires is based on nature of the template in hard template methods. The most typical, favorite and useful methods of hard template to synthesis Ag NWs are carbon nanotubes and nanoporous membrane. Thanks to hard template methods, synthesizing of Ag NWs can be done in a well-controlled manner[6].
1.3.1.1. Nanoporous Membranes

In this synthesis type, Ag NWs are grown in the membrane pores using nanoporous membrane as a template. With different pore sizes, diameter of Ag NWs can be verified. To create metals, conductive polymers, nanostructures and semiconductors with unusual small diameters, this method was used by research group of Charles R. Martin[7]. For the synthesis of metal nanostructures, porous alumina, porous polycarbonate, mesoporous silica and nanochannel glasses were be used. Thanks to hard templates, with chemical reduction of metal ions or electrochemically, extraordinary small sized nanostructures can be synthesized in a membrane. These methods are useful for the synthesis Ag NWs with well- defined and highly ordered morphology. The only disadvantages of this type of synthesis method is purification. During purification steps, nanowires can be damaged.[1]

1.4. Other hard template methods

Carbon nanotubes can be used as a good template for Ag NWs when filled with lead.[8] In this term, Ag NWs can be grown in the carbon nanotube template. Other method to fabricate Ag NWs is converting AgNO₃ to metallic silver by irradiation. In this term, electro microscope produce electron beam produced by electron microscope and AgNO₃ is irradiated with that electron beam. In this term AgNO₃ undergoes in this reaction :

\[ 2 \text{AgNO}_3 \rightarrow 2 \text{Ag} + 2 \text{NO}_2 + \text{O}_2 \]

After producing Ag⁰ ion in the reaction these reduced ions attract to silver rods for converting silver nanowires.

Deoxyribonucleic acid (DNA) is an unique participant of supramolecular interactions and its structure is also unique hence it is a gorgeous template for Ag NWs. [9] Silver cations has great interaction with DNA. In the DNA template, silver cations can be reduced via photoreduction [10][11] or reducing agent. There are some other hard template methods to synthesis Ag NWs; however, yield of synthesis is so low in this
types; also, hard template methods are limited in terms of their industrial applications and these methods are not scalable.

1.4.1.1. Soft Template Methods

Hard template methods have so many disadvantages to deal with them, scientists try to verify micelles, surfactants and polymers in soft templates which can dissolve in solutions. Thanks to dissolution potential of the soft template methods in the solution, they are applicable to the industry.

First of all, to synthesize inorganic nanowires and nano rods, cetyltrimethylammonium bromide (CTAB) is used as a surfactant. By using CTAB, perfect shape of silver nano rods and nanowires are synthesized. To grow anisotropic nanowires directly, rod like micro emulsions, surfactants and micelles are widely used in solution. In this method, NaBH₄ and ascorbic acid are used as the reductants. Growing crystals can absorb micelles, polymers and surfactants chemically and grow rates through desorption and absorption can be controlled kinetically. Nano spherical side products can be isolated from solution by centrifuged. Any soluble polymer such as hydrophilic block polymers[12], polyvinyl alcohol and polyethylene oxide[13] can be used as the capping agent and soft template; however, yield of Ag NWs solution might be low and the products might have irregular morphology, polycrystallinity and low aspect ratio. Due to these disadvantages of that, industrial applications of soft template is limited.[6]

1.4.1.2. Polyol Method

In polyol method, synthesized Ag NWs become both with high quality and large scale. This reaction is based on reduction of metal salt via polyol with heating. Polyvinyl pyrrolidone (PVP) is used to prevent aggregation of Ag NWs and as a capping agent during the whole reaction.[14] Xia’s group was the first research group who tried polyol synthesis for Ag NWs. During this experimental, they used platinum nanoparticles (Pt NPs) as seeds and ethylene glycol (EG) as both solvent and polyol.
In the first step Pt seeds was formed then Ag NWs was produced and PVP promoted an isotropic growth of Ag NWs.

Using Pt in this method is not suitable since Pt is expensive and synthesized Ag NWs include two different steps which limited application of polyol method to industry. That’s why same research group started to search self-seeding. This process did not need any other exotic seeds. Instead of using Pt seeds, they controlled the rate of injection of AgNO₃. They recognize that, ratio of PVP and AgNO₃ and degree of PVP have a great importance for the synthesis. The most important issue at this process is injection rate. Controlling the injection rate is critical to have accurate solutions at a large scale. [6]

Figure 1.1. Reaction Mechanism of Silver Nanowire

Figure 1.1. shows to synthesis reaction of Ag NWs. During synthesis procedure, firstly ethylene glycol is converted to acetaldehyde and hydrogen by heating. After this reaction, Ag⁺ ions in the Ag solution react with ethylene glycol to produce Ag⁰ atoms and di acetyl. PVP stabilize <100> faces which provides that reduced silver atoms can attracted to <111> face to provide growth in this direction.
1.4.2. Factors affecting the polyol synthesis of Ag NWs

1.4.2.1. Effect of Temperature

The temperature of the reaction while synthesis Ag NWs is so important. There is a critical point which enhances the synthesis. If the temperature is below that point, synthesis of high aspect ratio of Ag NWs is not possible which shows in Figure 1.2. When temperature is above 160 °C, conversion of the ethylene glycol to glycol aldehyde occurs according to this reaction:

\[
2\text{HOCH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow 2\text{HOCH}_2\text{CHO} + 2\text{H}_2\text{O} \quad [3]
\]

According to Figure 1.2., if the temperature of the reaction is in 110°C or 130°C, producing of silver nanowire is fair. In these temperature, just Ag NPs occur. If the temperature increases to 150°C, pure Ag NWs are synthesis so this is the critical temperature to synthesis Ag NWs. After this temperature amount of Ag ions can not be enough to react with acetaldehyde to produce Ag NWs. The diameter and length of the Ag NWs are showed in Figure 1.2.(g) and Figure 1.2.(h) These figures demonstrate that if temperature is increased more than 150°C, diameter of the Ag NWs suddenly decreased despite of increasing length. The diameter has an important role to use Ag NWs in industry so getting optimum value in diameter and length is essential.
Figure 1.2. SEM images of Ag NWs at different temperature (a) 110, (b) 130, (c) 150, (d) 170, (e) 190 °C, (g) changes in diameter of Ag NWs and (h) changes in length of Ag NWs at various temperature. [3]
Temperature is critical for synthesis of Ag NWs since formation of specific faces of silver depends on temperature. For example, when temperature is 110 °C micro sized silver structures occur instead of silver nanowires and silver rods. When the temperature increases to 150°C, twin particles form and their growing tendency into rod shaping increases.[15] When temperature becomes 160°C, thermal energy is enough to convert twin particles to nanowires with high aspect ratio. If temperature increases to more than 160°C, many silver rods occur in early steps; however, amount of Ag is not enough to create so many silver nanowires, that’s why, Ag NWs occurred with low aspect ratio and nanowires solution include a number of rods. [3]

1.4.2.2. Effect of NaCl Amount

NaCl is used as the catalyst in the reaction. When NaCl is added to reaction, Ag in AgCl compound reduces to Ag⁺ ions slowly. This slow reaction provides Ag nanoparticles to grow as multi twin particles, then these particles will be Ag nanowires. Without NaCl salt, Ag⁺ ions turn to Ag⁰ fast hence just Ag nanoparticles occur instead of Ag nanowires since Ag presents in an ionic medium in the solution.
Figure 1.3. SEM images of Ag NWs with adding different amount of NaCl. (a) 0, (b) 8.5, (c) 12, (d) 17.1, (e) 25.6 and (f) 85.5 µM. (g) shows XRD pattern of AgCl particles[3]
Figure 1.3. shows that amount of NaCl affects quality of Ag NWs. If correct amount of NaCl is not added to a solution, Ag NWs with high aspect ratio cannot be synthesized. Scanning electron microscopy (SEM) images of Figure 1.3. (a) show that in the absence of NaCl, Ag NWs cannot be synthesized. Instead Ag NPs occur. SEM images in Figure 1.3. (b) show that Ag NWs were formed; however, besides them micrometer sized Ag NPs were also formed. This demonstrates that there was not enough amount of AgCl. Reduction of Ag$^+$ ions to Ag$^0$ is fast; however due to insufficient AgCl, some Ag$^0$ ions turns to multi twins to produce Ag NWs while others grow as Ag micro particle forms. When all SEM images are examined, it is clear that proper amount of NaCl is necessary for the synthesis of Ag NWs with high aspect ratio. When amount of NaCl is enough, Ag NWs produced without micro meter sized nanoparticles. If amount of NaCl is higher than optimum amount, AgCl precipitates in the micron particle size. [3]

1.5. Conductive Inks

Printing media has a great attendance to create flexible and cost effective conductive ink towards unfriendly silicon based conductive inks. To print any ink, it has to have some strong physical and chemical properties.[1]

Surface characteristics, flowing ability on the surface, adhesion on the surface printed cohesion of ink and structure of dried ink are essential properties for the ink. Conductive inks can adapt to screen printing process easily since this liquid inks have low viscosity at high shear rate and high viscosity at low shear rate. [16]

1.6 Fabrication of Conductive Ink and Printing Process of Conductive Ink

Fabrication of adaptable conductive ink to the electronic devices has some restrictions about cost and flexibility. By dealing with these problems, excellent control is required on the magnetic, optical, electrical and thermal properties of the conductive ink to fabricate flexible and light weight devices. [1]
Electroplating methods are used to apply ink to any surface; however, these processes are expensive, need multiple steps and time consuming. Typically these methods are time consuming hence they so many steps and expensive. Screen printing methods are extensively used to transfer the ink to the surface of substrates of LCDs, LEDs, touch screens, solar cells, chemical and biochemical sensors; hence, this method has advantage in terms of time and cost [16]

1.7. Silver Nanowire Based Conductive Inks

To create conductive and optical transparent electrodes, most useful way is using long Ag NWs. Using thin and long Ag NWs provides an improvement in conductivity and transmittance in the device. If the length of the Ag NWs is around 10 µm, resistance of individual wires is 200-300Ω. By applying Ag NWs with Mayer rod technique, with 80% specular transmittance, 20Ω/sq and 8Ω/sq with 80% diffusive transmittance could be useful for solar cells [17].

By controlling composition of Ag ink, high conductive, high transparent and low haze Ag NWs based flexible electrodes can be fabricated. Kumar et al. fabricated this type of flexible films by Mayer rod technique with less than 300Ω/sq resistivity and more than 90% transmittance. Then they applied to their Ag NWs based thin films to the ITO [18].

Electrical conductivity, electrical resistance and magnetic properties of make Ag inks very handy to apply in basic electronic devices. Generally, silver inks includes different shapes like Ag nanoparticles (NP), nano rods, flakes, micrometer sized Ag. [19]. These particles can be dispersed in organic vehicles; however, they are not so stable in these solutions due to agglomeration and sedimentation and also adhesion properties of these particles are not so powerful. Instead of all these particles, using Ag NWs as a silver source in the paste provides high sintering and adhere ability to the surface. Moreover, in a network form Ag NWs are more transparent and conductive. Also bonding strength of Ag NWs to each other and mechanical
compliance of these nanowires are excellent. Due to all these reasons, using Ag NWs instead of Ag NPs is a better impact on the conductive paste. [19]

Ag inks can apply to surface of light emitting diodes (LEDs), light crystal diodes (LCDs), organic light emitting diodes (OLEDs), antenna, batteries, sensors, photovoltaic cells, radio frequency identification tags. [19]

1.7. Wearable Technology

Wearable technology becomes popular in these days in terms of its comfort, personal health and environmental friendly properties. This technology is useful for chest patches, eye glasses, headsets, chest bands etc. Also, in terms of flexibility, ultra-low devices have a great importance in medical industry. [20]

Wearable nano technological fabrics are soft, lightweight, thin and flexible so they can wear and use easily. Using nanotechnology in textile provides many advantageous. Firstly, placed sensors on the fabric can detect any natural electronic signals so pain on specific areas can cured with mild electro stimulation and gentle on body heating. Moreover, these fabrics have high quality design to wash and reusable. [21]

Many company focus on fabrication of wearable comfortable fabrics which breathe and move. Covering the fabric with thermoplastic polyurethane and using a flexible ink are so essential for fabrication of wearable technology.[22] Ink for wearable technology needs to cured below 120°C since above this point, most of the fabrics start to burn.[23]

1.7.1. Inks for Wearable Technology

Wearable electronic textiles become so popular day after day. They are known as electronic textiles (e- textiles) and considered to be very promising due to environmental advantages and excellent processing by digital fabricating techniques.[24] Printed flexible electronics have demonstrated great potential for further growth with the applications in health diagnostics [25,26] energy storage[27],
food security[28], touch screens[24], electronic paper[29], sensors[30][31], radio frequency tags and electronic textiles[32][24]. Wearable electronics (e-textiles) includes interconnections and electronics woven/knitted or printed/coated into textiles.[33] Wearable electronics are beneficial in terms of flexibility, lighter weight, comfortability and durability as well as maintaining the desirable electronic properties.[18][24] Ink jet technique is very useful for conductive silver inks and this technique has many beneficial over conventional manufacturing techniques like additive ad digital patterning, deposition of controlled quality of materials, reduction in material waste and compatibility with various substrates hence ink jet technique is one of the most promising method to fabricate of wearable and flexible electronics.[34][24] Due to strong healthy properties such as using as antioxidant in the body and conductivity abilities of silver NWs, they have great importance for fabricating conductive ink.
CHAPTER 2

EXPERIMENTAL

2.1. Silver Nanowire Synthesis

There are several methods for the synthesis Ag NWs such as DNA template, electrochemical technique, polyol process, hydrothermal method, chemical synthesis and ultraviolet irradiation method. In terms of cost and time, polyol method is the most efficient one. [3]

Cleaning all glassware is one of the most important parameters for synthesis Ag NWs; therefore, firstly all glassware were cleaned by alconox, deionized water, acetone and ethanol. After all cleaning procedures were done, the glassware were heated to 80 °C in a furnace and kept for 20 minutes.

2.1.1. Polyol Synthesis

Polyol method was used for synthesis Ag NWs. To have better control on the dimension of the Ag NWs, two different salts were used. One of them was sodium chloride (NaCl), other is copper chloride (CuCl2).

2.1.1.1. Polyol Synthesis with NaCl

In a typical polyol synthesis, 0.05 g NaCl, 1.77 g PVP (polyvinyl pyrrolidone) molecular weight [ Mwt ] : 55.000 and 80 ml EG (etylene glycol) were stirred in an erlenmeyer bulb at 90℃ and 1000 rpm. After observing a clear mixture, it was cooled down to room temperature. In the meantime, temperature of oil bath increased to 120 ℃ and 0.68 g AgNO3 in 40 ml EG was prepared at room temperature. PVP and AgNO3 solutions were mixed at 120 ℃. After mixing , temperature was increased to 160°C. Color of the solution was changed from transparent to nacreous gray. Once the
temperature of oil bath reaches to 160°C, reaction was let to stay at least 80 minutes in an oil bath while stirring in 1000 rpm.

![Photographs of the synthesis solution shows color change during synthesis Ag NWs by Polyol method with NaCl as the salt.](image)

In this process NaCl was used as the catalyst. After adding that salt, reduction of Ag\textsuperscript{+} ions to Ag became fast and AgCl was produced during this reaction. AgCl was useful for synthesis Ag NWs with high aspect ratio. During polyol reaction ethylene glycol (EG) was used as both solvent and reducing agent. It was converted to acetaldehyde by high temperature and acetaldehyde gave reaction with Ag\textsuperscript{+} ions to reduce them to Ag\textsuperscript{0} atoms. Source of the Ag was silver nitrate (AgNO\textsubscript{3}). Polyvinyl pyrrolidone (PVP) used as the stabilizing agent which stabilize <100> faces in the multi twin particles;
therefore, reduced Ag atoms can attracted to \langle111\rangle faces to grow the nanowires in this direction.

2.1.1.2. Polyol Synthesis with CuCl₂

In this type of Ag NWs synthesis, CuCl₂ was also used as the salt. PVP was used as the capping agent and solvent. Moreover; it was used to prevent aggregation of Ag NWs during the reaction. EG was used both as the solvent and reducing agent. By heating the solution, EG was converted to acetaldehyde which reacted with Ag⁺ ions in the silver solution. Using CuCl₂ as the salt in the reaction supplied to synthesis longer nanowires. The color of the solution changed with this order: Transparent color, black, pink, purple, gray and nacreous gray. Synthesis procedure of these Ag NWs was similar with polyol method by using NaCl as the salt. The difference between these two methods was type of the salt.

Figure 2.2. Photographs of the synthesis solution shows (a),(b),(c),(d),(e),(f),(g) and (h) demonstrate the color change of the solution which made by CuCl₂ as the salt.

In this method, 1.77 g PVP, 0.01g CuCl₂ and 80 ml EG were stirred at 90 °C and 1000 rpm. After transparent solution was obtained, this solution was mixed with 0.68 g AgNO₃ in 40 ml EG at 120 °C. The last solution was heated to 160 °C and when observing the change in color, solution was cooled to room temperature.
2.1.2. Purification of Ag NWs

Following synthesis Ag NWs by polyol process, solution was transferred to a beaker. Solution was let to rest for at least 3 days during this time, Ag NWs sink at the bottom while rods, Ag nanoparticles and others stayed at the top of the solution. After 3 days, most Ag NWs stayed at the bottom of beaker. Figure 2.3. shows the purification steps. After keeping synthesis Ag NWs at the room temperature, nanowires landed on the ground of the beaker the Ag NPs and other particles like Ag rods stay at the top of the solution. These particles were spilt then Ag NWs were purified by centrifuge. Firstly, they were centrifuged in acetone then in ethanol. After this step, they were dispersed in ethanol.

![Figure 2.3. Purification procedures for silver nanowires](image)

2.2. Materials

Salts are CuCl$_2$ and NaCl, n-methyl pyrrolidone (NMP) were purchased from Sigma Aldrich Chemical Co. Ltd. Weight average molecular weight of polyvinyl pyrrolidone (PVP) is 55.000. Polymer and AgNO$_3$ (99%) were purchased from Akerman Group Ltd. Carboxyl methyl cellulose (CMC), n-methyl pyrrolidone and glycerol were
purchased from Merck Chemical Co Ltd. Ethanol (99%) and acetone (99%) were purchased from Sigma Aldrich Chemical Co. Ltd.

2.3. Characterization of Silver Nanowires

Characterization of Ag NWs were done by various types of method. The most common one is scanning electron microscopy (SEM) which gives information about length and size distribution of Ag NWs. With a reliable SEM images, size and length ratio of Ag NWs can be also understood. The other method to characterize solution of Ag NWs is ultraviolet-visible spectroscopy (Uv-Vis). This spectrometric method provides information about density of Ag NWs.

2.3.1. Scanning Electron Microscopy (SEM)

The products of the polyol method were analyzed by Field Emission Scanning Electron Microscopy (FE-SEM) (Nova NanoSEM 430) operated at 10Kv voltage. SEM is a kind of microscope which scans the surface of the sample by beam of electrons. When electrons interact with the atoms on the surface of the sample, many signals about topography and composition of the sample are collected. Ag NWs solution in ethanol was sprinkled onto silicon wafer and dried at 120°C on the hot plate. Then wafers placed into SEM stubs with a carbon tape.

2.3.2. Ultraviolet Visible Spectroscopy (UV-Vis)

Absorbance of the capacity of the products of the polyol method were analyzed by Ultraviolet visible spectrometer (UV-Visible) (T80+ UV-VIS Instrument by PG Instruments Ltd.) at range between 300-800 nm. Range of UV is 190-400 nm and its for visible region is 400-800%nm. When halogen lamps and deuterium lamps are combined, absorbance value both in ultraviolet and visible ranges can be measured. Ethanolic solutions of Ag NWs were prepared into the quartz cells and placed into the UV-Vis cuvettes.
2.3.3. Four Point Probe

To measure resistivity of each region in a sample, four point probe was used. While resistance from end to end can be tested by digital multimeter, for a small area four point probe was used which gives information for each 1 mm/square.

2.3.4. LabMade Bending Device

Change in resistance of the samples with in the number of bendings were measured with lab made extensometer. The ink was spread on the fabric and it was placed between the arms of the extensometer for bending tests (Figure 2.4.). the extended distance were adjusted and test started.

![Picture of lab-made extensometer](image)

2.4. Formulation of Conductive Silver Ink

There are two ways to formulate conductive silver ink. One of recipes includes N-methyl pyrrolidone (NMP), glycerol, deionized water and ethanol while other was CMC and deionized water was based. Following fabrication of Ag inks, they can be
applied to fabrics, glasses or polycarbonate substrates. The important point of the substrates is cleaning. The surface of these substrates should be cleaned up before applying the Ag ink. Cleaning procedure of the substrates includes deionized water, acetone and ethanol. At least 10 minutes, the substrates are cleaned in these solvents in an ultrasonic bath. Only fabrics need another procedure for cleaning like using washing machine. To clean the fabric a washer was created (Figure 2.5.) and the fabric was cleaned in each solvent in this machine.

![Figure 2.5. Lab-made washing machine to clean all fabrics.](image)

### 2.4.1. Water Based Conductive Silver Ink

1.5 g carboxyl methyl cellulose (CMC) was stirred overnight in 25 ml of deionized water. CMC solution and silver nanowire suspension were mixed with 1:1 ratio and mixture was stirred at 60 °C in 500 rpm. Following fabrication of Ag ink, it was spread on to the fabric to measure resistance of it for an 1 cm and dried for 15 minutes in vacuum oven.
2.4.1.1. Long Ag NWs Based Ag Ink

To fabricate conductive silver ink, long Ag NWs were used. These nanowires were synthesized by polyol method using CuCl$_2$ as the salt. Using copper as the source of the salt provided formation of nanorods early during synthesis Ag NWs; therefore, synthesis of nanowires started earlier parts of the synthesis so long nanowires can be obtained. Then, these nanowires were used as silver sources in the ink. 40 ml of suspension Ag NW in ethanol was mixed with 12 gr CMC solution at room temperature and stirred at 70 °C 500 rpm for 10 hours. Following fabrication of a solid mixture, 5 ml of deionized water were added to that and stirred again at 500 rpm for 1 hour. This ink was applied to a fabric and a polycarbonate (PC) substrate via mask and dried in a vacuum oven for 20 minutes at 80°C.

2.4.1.2. Short Ag NWs Based Ag Ink

In a normal procedure of polyol method, NaCl was used as the salt. To synthesize Ag nanowires, NaCl was used theese nanowires were used as the Ag source in ink. 40 ml suspension of Ag NWs in ethanol was mixed with 12 gr CMC solution to produce a solid mixture. After 10 hours, solid mixture was obtained then ink was applied to a textile and a glass using mask and dried in the oven for 50 minutes at 80°C.

2.4.2. Organic Based Conductive Silver Ink

1.5 g polyvinyl pyrrolidone (molecular weight: 55000) was mixed with 20 ml N-methyl pyrrolidone (NMP), 25 ml ethylene glycol and 5 ml glycerol while stirred at 50 °C in 500 rpm. NMP solution was mixed with Ag NWs suspension with a 3:4 ratio. After preparation of silver ink, it was printed on the glass, textile and PET (polyethylene terephthalate) and dried in an oven.

2.4.2.1. Long Ag NWs Based Ag Conductive Ink

During fabrication of this ink, long Ag NWs were used which were synthesis by CuCl$_2$ as the salt. Ratio of Ag suspension and NMP solution was 1:1. Mixture of this solution
was stirred at 70°C 1000 rpm all night. After that it was applied to textile and glass using a mask, then they were dried in a furnace with for 20 minutes at 80°C.

2.4.2.2. Short Ag NWs Based Ag Conductive Ink

In this method, also Ag NWs suspension and NMP solution mixed with a ratio of 1:1. A similar procedure with CuCl₂ based conductive ink. Then the product ink was also applied on textile and glass. Afterwards the substrates were dried in furnace for approximately 30 minutes at 80°C.
3.1. Silver Nanowire Synthesis

Ag NWs were synthesized using two different salts which were NaCl and CuCl₂. Both salts affect the size of Ag NWs. Presence of Cl⁻ ion allow the synthesis of to have long Ag NWs. When using two Cl⁻ ions, length of Ag NWs becomes longer than the synthesized with ones Cl⁻ ion. That’s why, using copper chloride salt during silver nanowire synthesis provides extended nanowires. To understand size of Ag NWs, scanning electron microscopy (SEM) was used. Ag NWs were synthesis according to given procedure in Figure 3.1. First of all, 1.77 g PVP was mixed with 0.005g salt in 80 ml of EG at 90°C and 1000 rpm for 30 minutes. Following this step, mixture was cooled at room temperature. At the same time 0.68 g AgNO₃ was stirred in 40 ml EG at room temperature for 30 minutes. Then, these two solution were mixed at 170 °C for 80 minutes.

![Figure 3.1 Synthesis procedure of Ag NWs](image-url)
3.2. Polyol Synthesis

3.2.1. Polyol Synthesis With NaCl

Synthesis of Ag NWs by polyol method is the most useful and favorite method in terms of cost and time; therefore, only this method was used to synthesis the Ag NWs. By polyol method, single crystal Ag NWs can be synthesized in large quantities at relatively very low temperatures in the solution. There was a size distribution during the products of this experiment; however, mostly length of the Ag NWs were around 10-15 µm. Synthesis Ag NWs were purified using acetone and ethanol at several times by centrifuge.

SEM images of NaCl based Ag NWs were shown in Figure 3.3. These images demonstrates that amount of silver nano rods, silver nanoparticles and others is low; therefore, synthesis of pure Ag NWs were successful. As can be understood from Figure 3.2, there were length and diameter distributions; however, the range of that was not so extensive.

Figure 3.2. (a) Graph of length distribution of Ag NWs which were synthesized by using NaCl as a salt. (b) Graph of diameter distribution of Ag NWs which were synthesized by using NaCl as a salt.
3.2.2. Polyol Synthesis With CuCl$_2$

Using NaCl as the salt causes synthesis short Ag NWs so instead of NaCl, CuCl$_2$ was used as the salt in this part. During the synthesis Ag NWs by CuCl$_2$, color of the solution changes from transparent, black, pink, purple, gray and gray. Before synthesis of Ag NWs, pink and purple color were obtained due to Ag NPs. The color of the particles via CuCl$_2$ was different than the color of the particles via NaCl since diameter size of the particles are not same. Nanoparticles have different colors with different size as shown in Figure 3.5. [35]
Using copper as the salt causes synthesis Ag NPs with large diameter and this NPs are converted to long Ag NWs. The change in diameter size can be understood from the color of the solution as shown in Figure 3.4. If the color is orange, particles are large; however, if the color is pink or purple, size diameter of the particles was smaller. Figure 3.5 gives information about the distribution of length and diameter. Using CuCl₂ as the salt during synthesis Ag NWs supplies longer nanowires with 45-50µm; hence, distribution of them is still not so great.

**Figure 3.4. Picture of Ag NPs with different size [35].**

**Figure 3.5. (a) Graphs of length distribution of Ag NWs which were synthesized by using CuCl₂ as a salt.**

(b) **Graphs of diameter distribution of Ag NWs which were synthesized by using CuCl₂ as a salt.**
Figure 3.6. (a), (b), (c) and (d) are SEM images of Ag NWs which were synthesized by using CuCl$_2$.

SEM images of Ag NWs in Figure 3.6 demonstrates the length of the solution. Despite there is so long Ag NWs, solution does not be seemed so pure; hence, there are a length distribution and also soma nano rods are observed in the images.

3.2.3. UV results of each solution

There are three different kinds of Ag NWs solutions which were made by different ratio of AgNO$_3$ and PVP and also various types of salts; NaCl and CuCl$_2$. 
Figure 3.7. UV Visible graph of Ag NWs which were synthesized by using NaCl.

In this method of synthesis of silver nanowire, 0.68 g AgNO$_3$ and 1.77 g PVP were used. Molar ratio of PVP: AgNO$_3$ was 3:400. NaCl was used as the salt in this method. According to UV results of these nanowires, two peaks were observed and one of them belongs to quadrupole mode and other is longitudinal.[36] One of them shows the diameter while other shows length. This graph is like a proof of the SEM images since in these images, also these two properties of Ag NWs are obtained.
Figure 3.8. UV visible graph of Ag NWs which were synthesized by using CuCl$_2$

The graph in Figure 3.8 gives information about absorbance of CuCl$_2$ based Ag NWs. Ratio of PVP: AgNO$_3$ was the same with the sodium based Ag NWs; however, concentration of these two are not the same. Despite concentration of copper salt in the synthesis Ag NWs by CuCl$_2$ as the salt is half of the sodium salt in the synthesis Ag NWs by NaCl as the salt, absorbance of both were not so different. It shows that Cu based nanowires have longer lengths hence they have similar absorbance range though their low concentration.

While silver nanowires absorb the light, surface electrons undergo polarization due to electromagnetic ability of the light. For that matter, characteristic surface plasmon oscillation occurs. Figure 3.7. and Figure 3.8. refer to Ag NWs in ethanol. These figures demonstrate two sharp peaks and one of them belongs quadrupole while other peak belongs longitudinal [36]. These two peaks are proof of two dimension of the Ag NWs. Despite Ag NWs are 1D structures, they have two dimension for length and diameter [36].
3.2.4. Silver Nanowire Based Conductive Silver Ink

Four different types of conductive silver inks were prepared. Two of them were fabricated using NaCl as the mediator while other synthesized using CuCl₂ as the mediator. N-methyl pyrrolidone and carboxy methyl cellulose were adhesion chemical of these conductive Ag inks.

3.2.4.1 Long Ag NWs based Conductive Ag Ink

The Ag NWs which used in this ink were synthesis by using CuCl₂ as the mediator. Formatted Ag ink with these nanowires were applied to a fabric, then dried in the oven. After that, flexibility of this fabric was tested with lab-made bending device.

<table>
<thead>
<tr>
<th>Number of Cycle</th>
<th>Resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.7040</td>
</tr>
<tr>
<td>200</td>
<td>0.6620</td>
</tr>
<tr>
<td>400</td>
<td>0.6590</td>
</tr>
<tr>
<td>600</td>
<td>0.7421</td>
</tr>
<tr>
<td>800</td>
<td>0.7721</td>
</tr>
<tr>
<td>1000</td>
<td>0.8172</td>
</tr>
<tr>
<td>1200</td>
<td>1.1137</td>
</tr>
<tr>
<td>1400</td>
<td>1.0673</td>
</tr>
</tbody>
</table>
Table 1 and Figure 3.9. show that bending did not have a bad effect of this ink. In the first 200 cycles, there was a decrease in the resistivity of ink; however, after this point resistivity increases and keeps this value for a long time. Reason of first decreasing is related to the fabric. Most probably after first 200 bending, ink attached to each hole of fabric hence there was nearly no change in resistance of the ink.
After applied Ag ink to the fabric, different voltages were applied to the fabric to examine heating temperature of the ink. The results of applying voltage gives in Figure 3.11.
These figures show that until 125 °C, silver ink can heat the fabric. After that temperature, fabric was burned; otherwise, heating process may continue. When comparing the temperature and current Figure 3.11 (a), it is clear that resistance did not change with changing current and it is similar for the graph in Figure 3.11 (b). Therefore, applying the voltage to ink, caused a change in current and temperature; however, the resistance of the ink did not change.

### 3.2.4.2 Short Ag NWs Based Conductive Silver Ink

Ag NWs of this ink was synthesis by NaCl as the mediator. These types of nanowires are not that long. Lengths were between 10-15 µm. This ink was fabricated with these NWs and CMC. After fabricated Ag ink, it was printed to a textile, then voltage was applied to the fabric to examine heating ability of Ag ink.
These figures are similar to those of Figure 3.10, which demonstrates that this ink also can be heated to 125 °C which is temperature that the fabric starts to burn.

*Figure 3.13. (a) Bended position of the fabric, (b) Stretched position of the fabric and (c) After printing on the fabric and dried Ag ink in oven*
Table 3.2. Change of resistivity of NaCl based conductive Ag ink toward bending cycles.

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>Resistance (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.780</td>
</tr>
<tr>
<td>200</td>
<td>6.0300</td>
</tr>
<tr>
<td>400</td>
<td>9.2000</td>
</tr>
<tr>
<td>600</td>
<td>10.220</td>
</tr>
<tr>
<td>800</td>
<td>13.590</td>
</tr>
<tr>
<td>1000</td>
<td>14.400</td>
</tr>
<tr>
<td>1200</td>
<td>16.740</td>
</tr>
<tr>
<td>1400</td>
<td>15.600</td>
</tr>
</tbody>
</table>

Figure 3.14 Graph for resistance of NaCl based Ag NWs with respect to number of bending cycles.
Table 3.2 and Figure 3.14 demonstrate the change in resistance of the ink on the fabric. As mentioned before in Table 3.1, after first 200 cycles, resistance decreased then increased again which shows that in the first part fabric and ink were combined further, then due to increasing number of bending, resistance started to increase.

3.2.4.3. CuCl$_2$ based Ag NWs and NMP Based Silver Ink

NMP based solution was used in this type of ink. NMP is a good adhesive for polymers and it was mixed with long nanowires. After fabricated this ink, it was applied to both to fabric and polycarbonate substrates.

Polycarbonate is very soluble in ethanol, chloroform, acetone, isopropanol and toluene. These five solvents are the basic solvents of nearly used in all silver inks in the industry. To apply an ink to the polycarbonate base, solvent of this ink should not dissolve the polycarbonate. Lots of researches show that, polycarbonates are not soluble in deionized water. At this point, this ink is so useful to apply the polycarbonate sample.

Long nanowire, NMP and deionized water based ink was fabricated then applied to a polycarbonate base and printed on a fabric using a mask. The applied difference between these inks is solvent. The solvent of fabricated ink was deionized water while the solvent of commercial ones were toluene, chloroform, acetone or ethanol. When water based ink was applied to polycarbonate, there was not any damage on the surface of polycarbonate; while others applied to the polycarbonate, surface of them were damaged due to reaction of polycarbonate and the solvent in Figure 3.15.
Photos of the PC substrates in Figure 3.15. part (c) and (d), it was clear the damage effect of the inks to polycarbonate are shown. In 3.15. (c), fabricated silver ink was applied to polycarbonate and the surface of the polycarbonate was kept as smooth while Figure 3.15. (d) after applying commercial Ag ink to the polycarbonate, smoothness of the surface was damaged and corners of the polycarbonate were curled.
Due to solvent of the ink, polycarbonate dissolved a little bit hence shape of polycarbonate base was changed. It was more obvious at picture of thin one which is Figure (d). When this ink was applied to 3 cm polycarbonate, solvent of the ink caused some cohesion on the surface of the polycarbonate since this polycarbonate was easily dissolved in the solvent.

After this ink worked for polycarbonate, it was printed onto fabric. Then the fabric was heated until the burn.

![Figure 3.16](image)

*Figure 3.16. (a) Changing in current with various temperature. (b) Changing in voltage via different temperature.*

This fabric was heated until 125 °C due to same reasons with others which was temperature of burning the fabric. As mentioned in Figure 3.11, with the changing voltage, resistance of the ink was not changed so this ink is also durable.
Figure 3.17 (a) bended position of the fabric, (b) stretched position of the fabric and (c) after printing on the fabric and dried Ag ink in oven

Although this did not seem so homogeneous, its resistance during the change in stretchability did not change much.
Table 3.3 Change of resistivity of CuCl$_2$ and NMP based conductive ink toward bending cycles.

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.62</td>
</tr>
<tr>
<td>200</td>
<td>5.32</td>
</tr>
<tr>
<td>400</td>
<td>5.03</td>
</tr>
<tr>
<td>600</td>
<td>5.22</td>
</tr>
<tr>
<td>800</td>
<td>5.12</td>
</tr>
<tr>
<td>1000</td>
<td>5.87</td>
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<tr>
<td>1200</td>
<td>5.76</td>
</tr>
<tr>
<td>1400</td>
<td>5.22</td>
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<tr>
<td>1600</td>
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<td>5.74</td>
</tr>
<tr>
<td>2600</td>
<td>5.48</td>
</tr>
</tbody>
</table>
According to Table 3.3 and Figure 3.18, resistance of the ink did not depend on number of the bending cycle. Although number of cycle increased, conductivity between ink and fabric did not change hence resistivity also did not change.

### 3.2.4.4. Short Ag NWs and NMP Based Silver Ink

This types of inks include short Ag NWs by NaCl as the salt and NMP as the adhesive. After fabricating this ink by mixing NaCl based Ag NWs and NMP solution, it was applied to the fabric.
Figure 3.19. (a) Changing in current with various temperature. (b) Changing in voltage via different temperature.

These two figures demonstrate that the burning this ink has a great tolerance to heating. Like the results of Figure 3.11 and 3.16, resistance of the fabricated ink does not change with changing voltage. Although temperature was increased to 125°C, just fabric was damaged and form and shape of the ink were kept.
Although this also did not seem so homogenous, resistivity was equal at each point of this ink.
Table 3.4. Change of resistivity of NaCl and NMP based conductive Ag ink with respect to bending cycles

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.62</td>
</tr>
<tr>
<td>200</td>
<td>22.32</td>
</tr>
<tr>
<td>400</td>
<td>22.03</td>
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<td>21.87</td>
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<td>1200</td>
<td>21.76</td>
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<td>23.22</td>
</tr>
<tr>
<td>1600</td>
<td>23.22</td>
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<tr>
<td>1800</td>
<td>23.81</td>
</tr>
<tr>
<td>2000</td>
<td>24.12</td>
</tr>
<tr>
<td>2200</td>
<td>23.92</td>
</tr>
<tr>
<td>2400</td>
<td>24.74</td>
</tr>
<tr>
<td>2600</td>
<td>24.48</td>
</tr>
</tbody>
</table>

Figure 3.21. Graph for resistivity of small Ag NWs and NMP based Ag NWs towards number of bending cycles.
These results show that resistivity of this ink did not change with the increasing number of bending. That is a good point since this ink can be applied to textile industry easily.

Figure 3.22 (a) Photograph of bended position of the fabric, (b) Photographs of stretched position of the fabric and (c) Photographs of after printing on the fabric and dried Ag ink in oven.
Table 3.5: Change of resistivity of industrial conductive Ag ink toward bending cycles

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>200</td>
<td>0.27</td>
</tr>
<tr>
<td>400</td>
<td>0.35</td>
</tr>
<tr>
<td>600</td>
<td>0.28</td>
</tr>
<tr>
<td>800</td>
<td>0.37</td>
</tr>
<tr>
<td>1000</td>
<td>0.60</td>
</tr>
<tr>
<td>1200</td>
<td>1.35</td>
</tr>
<tr>
<td>1400</td>
<td>1.38</td>
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<tr>
<td>1600</td>
<td>1.52</td>
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<tr>
<td>1800</td>
<td>1.53</td>
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<tr>
<td>2000</td>
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<tr>
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</tr>
<tr>
<td>2400</td>
<td>1.53</td>
</tr>
<tr>
<td>2600</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Figure 3.23: Graph for resistivity of commercial conductive Ag ink with respect to number of bending cycles
According to Figure 3.22., after applying commercial ink to the fabric, it seemed so homogenous and resistivity of the ink toward bending cycles was measured. Table 3.5. and Figure 3.23 demonstrate that, after 1000 bending cycles, resistivity of the ink changed nearly two times more. Therefore, the fabric which commercial ink was applied on, is not durable after 1000 bending cycles.

The commercial ink includes Ag NPs while our inks includes Ag NWs. This is yet another important effect to apply the ink at a specific surface since Ag NWs has a good adhesion to the surface thanks to its longer length and larger area than Ag NPs. Also nanowires are more conductive, have excellent mechanical compliance, bond strength of them can be improved so easily in a network form.
In this thesis, Ag NWs were synthesized by different types of salts by polyol method. To fabricate the Ag ink, these nanowires were used and the effect of length of nanowires and types of adhesive on the ink were studied. In the first part of this thesis, synthesis of Ag NWs was discussed. Some details in polyol process to synthesize Ag NWs were given, then some parameters like amount of NaCl were mentioned. Also, the effect of using CuCl$_2$ instead of NaCl as the salt was discussed. Then all the synthesized nanowires were used to form an Ag ink. To form a good Ag ink, two different adhesives were used: one of them is CMC and the other is NMP. The effect of adhesives was demonstrated by printing the ink into a fabric. Moreover, applying the ink to a polycarbonate substrate is a problem in the industry. To deal with this issue, solubility of polycarbonate was studied and if the solvent of an ink was chloroform, toluene, ethanol or any chemicals like them, this ink was not suitable for polycarbonate. The fabricated water based Ag ink and organic based Ag ink by using deionized water as the solvent were found to be applicable for polycarbonate since it did not damage the surface of the samples.
REFERENCES


