Highly Conductive Silver Flake/nanowire Composites Inks and 3D Printing Processing in Flexible Electrodes Application

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Abstract

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Nowadays, conductive ink has attracted our attention in research and industry due to their popularity in printed electronics. Among various conductive inks, silver ink has been explored deeply and widely because its high conductivity and stability. However, with the requirement of different printed electronics especially flexible electronics, good mechanical properties become more and more important. Most researcher focus on how to formulate silver inks with high conductivity and good mechanical properties. In this report, high conductive silver flake/nanowire composite is formulated and characterized with various instruments. A simple method to modify the contact of flakes with silver oxide nanoparticles is introduced to further improve the conductivity of silver inks. The function of silver nanowires in silver inks to increase the flexibility of silver electrodes is illustrated in detail. Also, the process of printing
silver inks on curved surface with good resolution by 3D printer has been explored and a variety of printing parameters were studied.
1. Introduction

1.1 Overview

With the development of technology, electronics has experienced dramatic changes from techniques to applications. More and more smaller, better and faster electronic devices can be achieved and applied to our daily life.\textsuperscript{[1]} However, traditional technology limits the flexibility, complexity and practicality of electronics. Since Teng and Vest\textsuperscript{[2]} produced metal conductors for solar cells with inkjet printing, printed electronics which can overcome the limitations of traditional technique attracts significant attention from the scientific community and industry.\textsuperscript{[3]}

Printed electronics combines various inks with printing technologies to produce large-scale, low-cost and diverse electronic devices and systems such as semiconductor,\textsuperscript{[4,5]} insulting layers,\textsuperscript{[6,7]} conductive layer\textsuperscript{[8,9]} and biological active layers.\textsuperscript{[10,11]} Recent years, new applications in electronics/optics fields such as solar cells,\textsuperscript{[12]} logic circuits,\textsuperscript{[13]} radio-frequency identification (RFID) tags,\textsuperscript{[14,15]} and sensors\textsuperscript{[16]} arise resulting from the diversity of printing technology and inks.

Among various ink, conductive ink plays an important role in this field due to its’ novelty in being applied to printed circuit boards, flexible aerospace and automotive components, conductive grids for flexible displays screens, medical devices and bio-sensors, as well as energy-related components like electrodes in solar cell, current collectors in flexible batteries.\textsuperscript{[17,18]} Conductive ink is a multi-component system that contains a conducting materials in a liquid vehicle and various additives that enable optimal performance of the whole system, including the printing device and the substrate.\textsuperscript{[19]} Different application asks these ink to meet specific requirements in terms of processing temperatures, cost, performance, stability, energy efficiency and so on. Therefore, there are different conductive inks to satisfy our need. According to the selection of main precursor, conductive ink can be divided by three types: polymer based ink,\textsuperscript{[20]} metal based
ink\textsuperscript{[18]} and carbon based ink.\textsuperscript{[21]} Compared with other inks, metal-based ink has its own prominence in terms of conductivity. As we all known, silver is the most conductive metal in nature, and silver oxide is also conductive unlike the oxides of other metals, which results in the deep study and research of conductive silver ink. Fundamentally, there are three steps involved in form a silver conductive layer (Fig.1).

\textbf{Figure 1.} (a) Applications of conductive silver ink; (b) Representation of the process involved in the formation of silver conductive layers. Reproduced with permission from [ref. 17]

\textbf{Figure 2.} Representation of the composition of conductive silver ink.
1.2 Conductive Silver Ink

The diversity of silver component that can be used to compose ink has expanded dramatically over the past decade. As shown in Fig.2, conductive silver ink is composed by three parts: solvent, silver components and binders. Nowadays, according to the different silver components, conductive silver ink can be divided into two categories. One is silver organic decomposition ink. The other is silver particles ink.[1]

For silver particles ink, a significant effort has been devoted to the production and utilization of silver particles of different morphologies (e.g. nanoparticles, nanowires, flakes, etc.) due to the influence of conductivity and mechanical behavior such as flexibility, stretchability and so on. This ink generally contains three parts: (i) silver micro- and/or nanoparticles, (ii) organic binder/additive and (iii) solvent.[22]

Silver micro- and/or nanoparticles is main component of ink, which directly influence the properties of final products. In the process of forming conductive film, neighboring silver particles need to be in contact with each other to form a conductive network throughout the matrix of polymers. According to literature, the dispersion, specific surface area and loading density of the silver particles are relative to the quality of network to impact the conductivity. The optimization of these parameters is an important process in silver ink formulation. For example, Luo et al.[23] investigated that dispersibility of silver particles strongly affects the microstructure of thick film and electrical performance of conductive paste in solar cells. These years, silver nanowires have attracted interest for electronic application especially transparent conductors. Silver nanowire networks have excellent mechanical compliancy due to the large length-to-diameter aspect ratio of AgNWs. Therefore, AgNWs becomes a potential candidate for conductive component to achieve printable and stretchable conductors. For example, Pei et al.[9] developed a water-based
silver-nanowire screen-print ink for the fabrication of stretchable conductors and wearable thin-film transistors. With so many different morphologies of silver particles, we can make a choice depending on applications.

Organic binder is used to promote particle wetting, film formation, and adhesion substrate. It also adjusts rheological behavior and viscosity of ink to meet the requirement of printing process. On the other hand, other organic additives such as dispersive agent that help the dispersion of silver particles, antifoaming agent which prevent foam formation during mechanical agitation and so on. All above organic components are responsible to the quality of inks and conductive films. According to the nature of solvent and silver particles, there are hundreds of organic binders and additives to satisfy our needs.

Considering solvent selection, there are two different conductive silver ink solvent-based and water-based ink. In the beginning, we use common non-aqueous solvent such as ethers, acetates and glycols, which provide good rheology, adhesion and flexibility. However, it has been demonstrated that the use of volatile organic compounds results in the coffee-ring effect which is detrimental for printed electronics. It has been noted that the use of a binary mixture of solvents can suppress the effect if one of the solvents has a much higher boiling point than the other.[24,25] Nowadays, more and more researchers devote to form water-based silver ink due to its environmental friendliness. For example, Blayo et al.[22] formulated water-based silver pastes that adapted for screen printing with different silver contents (67-75%) for electronic applications. No matter what kind of solvent, boiling point, volatility of solvent and wettability of silver particles are three main criterions when we choose a suitable solvent. These properties influence the following printing and post-printing treatment process largely.
While silver particle inks have been adopted commercially, silver organic decomposition ink attracts our interest recently. Silver organic decomposition ink which replaces silver particle with silver organic precursor is a solution-based ink and provides a number of advantages.\cite{26,27} Unlike silver particle ink, which require a high temperature treatment to form conductive network, their conductive patterns are formed directly by a thermal decomposition reaction of silver precursor under mild conditions, which means we can get high conductivity at a lower temperature than that of required for the silver particle inks. This advantage expands the application of silver ink especially in flexible electronics. On the other hand, the ink is easier and suitable for printing process because it is solution. Some common problems such as nozzle clogging in inkjet printing will be avoided, which allows feature of extremely fine resolutions to be printed.

An optimal silver organic decomposition ink should meet such requirements as simple synthesis procedure, low viscosity, high silver content, high conductivity of the patterned features, mild processing temperatures, and long-time stability, etc.\cite{28} Nowadays, most researchers focus on appropriate silver organic precursor, which can be decomposed at low temperature and obtain high performance. For example, Dearden et al.\cite{29} synthesized a silver-organic ink for use in a drop-on-demand ink-jet printer. They prepared the ink by dissolving a synthesized silver carboxylate into xylene. They found that resistivity value drops down to values of 2 to 3 times the theoretical resistivity of bulk silver after curing at 150°C. Jahn et al.\cite{30} discussed the utilization of one metal organic silver salt for the formulation of an aqueous silver organic decomposition ink suitable for inkjet patterning of conductive features on glass and flexible substrate materials such as PET by applying thermal or photothermal treatment. Finally, the conductivity of silver features on glass and PET substrates are 43% and 18% of the bulk silver conductivity, respectively.
1.3 Printing Techniques for Silver Inks

Due to the variability of silver inks, it can be printed by various techniques. Some popular techniques are discussed below in detail.

1.3.1 Screen Printing

In the beginning of the 20th century, screen printing, a very versatile printing technique which allows for two-dimensional patterning of printed layer, firstly developed.[31] Fig.3 illustrates the operating principle of screen printing. Its main characteristic is a requirement for a relatively high viscosity and a low volatility of the ink. It is a simple and low-cost printing technique which can be used to print a wide variety of materials on various substrates such as glass, PET, silicon, etc. Furthermore, wide range of thickness of films can be achieved by adjusting the stencil’s thickness.

![Illustration of the screen-printing process](image_url)

**Figure.3** Illustration of the screen-printing process (above) and examples of a laboratory screen printer (bottom left) and an industrial screen printer (bottom right). Reproduced with permission from [ref. 31]
1.3.2 Ink Jet Printing

**Figure.4** Schematic illustration of the ink jet printing process (a) drop-on-demand system; (b) continuous drop system. Reproduced with permission from [ref. 31]

Unlike screen printing, ink jet printing is a novel method in the beginning.\textsuperscript{[17,31]} Ink jet printing is deemed to be one potential and interesting technique for industrial printing process. Recently, industrial ink jet printer has been commercially available, which lead to researchers’ enthusiasm on this area. Compared with other all printing techniques, it can deposit a broad range of ink with quite high-resolution pattern accurately and rapidly in a large area at low cost. It is worthy noted that ink is ejected into substrate, which means printing head doesn’t contact with substrate.\textsuperscript{[12]} The most important feature of ink jet printing is controllable nozzle which can spray ink from the tip to substrate as we setting. There are two modes for droplet formations in printing process, which are shown in **Fig. 4.**\textsuperscript{[31]}

**Fig.4**(a) describes the drop on demand (DOD) system where droplets are generated on demand from a nozzle by using a data pulse strain via a pressure transducer. **Fig. 4**(b) is another system which generates droplets continuously and controls the droplet direction by deflector. Due to the principle of systems, it put forward some restrictions on the ink formulation. Unlike screen printing,
which requires high viscosity ink, ink jet printing requires silver ink with low viscosity (4-30cP). Additionally, high surface tension (>35 mNm\(^{-1}\)) that is beneficial to the formation of droplet is necessary.\[^{31}\]  

1.3.3 Flexographic Printing

Flexographic printing is a R2R technology and relies on the transfer of ink. \textbf{Fig. 5} illustrates the system of this printing process which is achieved by four rollers. At first, fountain roller transfer ink to anilox roller that is embedded with engraved cells/micro cavities. Then, the ink is transferred to the roller with printed pattern that performs the final transfer to the web, which is controlled by an impression roller.\[^{31}\] From an industrial point of view, flexographic printing satisfies high resolution requirement of flexible electronics such as OLED and thin film transistors. Conductive silver ink works better on this printer.

\textbf{Figure.5} Illustration of the flexographic printing process. Reproduced with permission from [ref. 12]
1.3.4 Micro-dispensing Printing

All above techniques we discussed are fit to planar or flexible substrate. Conductive ink can also be printed on 3D surface by micro-dispensing printing process.\cite{32,33} The primary advantages of this process are flexibility and controllability. Except for the formation of high resolution complicated pattern on 3D surface, it has no strict restriction on ink’s viscosity and can be applied to many different inks such as conductive inks, solders, and dielectric paste etc. Moreover, besides the basic adhesion requirement, this system can print on thousands of substrates. Finally, micro-dispensing printing is a digital process, which means we can adjust and control the whole printing process easily and rapidly. Fig. 6 shows the principle of micro-dispensing printing process.\cite{33} The ink is extruded from nozzle that is closed to the substrate by different technologies such as the rotary micro-valve dispenser technology and form specific patterns. There are some important parameters for this process: printing speed, extrusion speed, distance between nozzle head and substrate, and valve positions. These parameters mostly relate to the final patterns’ quality.

![Figure 6 Principle of micro-dispensing printing process. Reproduced with permission from [ref. 33]](image)
1.4 Post-printing Treatment

For high electrical conductivity, post-printing treatment is necessary to sintering silver together and reduce the interface of silver particles to form continuous metallic contact and get high conductivity. Sintering is the process of welding and compacting silver particles together without melting it.[19] The most common and conventional method is thermal sintering. With the surface-to-volume ratio increase, self-diffusion of the silver metals increases which lead to the descend of melting point as compared to bulk metal.[34]

In addition to thermal sintering, several new methods are applied to sinter such as photonic sintering,[35] plasma sintering,[36] microwave sintering,[37] electrical sintering.[38] Different method is suitable to different silver inks and films. Therefore, choosing matched sintering method is an important step for conductive silver films.

1.5 Current Challenges on Conductive Silver Ink

1.5.1 Conductivity

Nowadays, the study on conductive silver ink focus on good conductivity with good mechanical properties such as flexibility. In the formation of conductive silver films, a 3D continuous conductive network is built by silver particles. The total conductivity consists of the conductivity of the polymer matrix, silver material (i.e. silver particles), surface resistance of the silver.[26] Normally, polymer matrix’s conductivity can be neglected due to small contribution to the whole conductivity. Therefore, the properties of silver network results in the conductivity mostly, which was directly influenced by the silver content loading and post-printing process. It is known that higher silver content loading can obtain more compact silver film after solvent is gone, which helps to get continuous conductive network easily. Post-printing process impact the quality of contact
between silver particles. If this contact is physical contact, a contact resistance will generate which contributes to high overall resistance. There are two methods to avoid contact resistance. One is use larger silver particles to reduce the number of contact points to decrease the whole contribution of physical contact. Another method is to transfer physical contact to ohmic contact through post-treatment method such as sintering. Although higher curing temperature is beneficial to the formation of ohmic contacts to form a better conductive network, with the increasing need of flexible electronics, whose substrates are polymer that are heat sensitive, how to achieve high conductivity with low curing temperature is the main challenge in this area. There are several ways to overcome this challenge:

(1) In section 1.2, we know that the main advantage of silver organic decomposition ink is that we can get relative high conductivity at low temperature due to the requirement of decomposition reaction. But the limited precursors and complicated systems increase the difficulty of commercially available.

(2) For silver particles ink, most researchers use silver nanoparticles as conductive component which own low sintering temperatures resulting from small size. However, this method is still restricted by the high cost on nanoparticles synthesis. On the other hand, because all silver nanoparticles have organic insulating materials on their surface, in comparison with silver nanoparticles, higher temperature is required to remove these organic materials.

(3) Nowadays, there are some commercially available low-temperature silver ink that composed by silver micro-flakes with appropriate solvents and binders. They can get relative good conductivity at relative temperature (120-200°C).
Based on above discussion, Table 1 lists the conductivity of some reported publications and commercial silver inks at low sintering temperature. We can know that the highest conductivity silver ink is $1.11 \times 10^5 \text{ S cm}^{-1}$ for the silver ink produced by NovaCentrix.

Table 1. Comparison of electrical conductivity of the present work with various previous research and commercial silver ink

<table>
<thead>
<tr>
<th>Solid contents</th>
<th>Substrate</th>
<th>Sintering temperature [°C]</th>
<th>Sintering time [min]</th>
<th>Electrical conductivity [S cm$^{-1}$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver flake 70 wt%</td>
<td>Paper</td>
<td>160</td>
<td>50</td>
<td>$5.26 \times 10^4$</td>
<td>[26]</td>
</tr>
<tr>
<td>Silver NPs 60 wt%</td>
<td>Glass</td>
<td>200</td>
<td>60</td>
<td>$3.30 \times 10^4$</td>
<td>[39]</td>
</tr>
<tr>
<td>Silver 68 wt%</td>
<td></td>
<td>130</td>
<td>4</td>
<td>$2 \times 10^4$</td>
<td>AG-959 Conductive Compounds Inc.</td>
</tr>
<tr>
<td>Silver 80 wt%</td>
<td></td>
<td>170</td>
<td>30</td>
<td>$2.22 \times 10^4$</td>
<td>9169 Dupont Inc.</td>
</tr>
<tr>
<td>Silver NPs 44 wt%</td>
<td>Polyester</td>
<td>140</td>
<td>1.5</td>
<td>$1.11 \times 10^5$</td>
<td>PSI-211 NovaCentrix</td>
</tr>
<tr>
<td>Silver flake 65 wt%</td>
<td>PET</td>
<td>150</td>
<td>30</td>
<td>$1.11 \times 10^5$</td>
<td>HPS-021 NovaCentrix</td>
</tr>
</tbody>
</table>

1.5.2 Flexibility

Recent years, flexible electronics becomes hot topic research field gradually. The mechanical flexibility and stability of the silver film is our main focus. The flexibility is influenced by the quality of silver films. If the film can resist the damage from bend and don’t form crack, this silver film has good flexibility. Therefore, how to improve the ability of resisting bend force is the main challenge. As we mentioned before, conductive networks are composed with polymer matrix and silver particles. There are two ways to improve the flexibility of silver ink:

1. Using silver nanowires as main silver component. Due to the large length-to-diameter aspect ratio of AgNWs, the AgNWs network have excellent mechanical compliance compared with other silver components.
(2) Choosing appropriate polymer system can also improve the flexibility of silver film. Because a good polymer matrix benefits to stand the bend force. However, due to the complexity of polymer system, how to form a good polymer matrix need further study.\textsuperscript{[9,14]}

1.6 Scope of Project

Our project focus on highly conductive (resistivity on the order of $10^{-6}$) silver nanowire/particle composites inks and 3D printing processing flexible electrodes application.

First, we chose silver micro-flakes as main silver component that requires relative low curing temperature and are easier to be wetted compared with nanoparticles. Compared with silver compounds, it owns higher conductivity that is closed to bulk silver. In addition, not like silver nanoparticles, using micro-flakes can reduce the amount of contact points between flakes, which can reduce the contact resistance that we mentioned before. Moreover, to get excellent flexibility, we synthesized silver nanowires and add it to our ink to formulate silver flakes/nanowires composite ink. As we all know, silver nanowires have excellent mechanical compliancy result from the large length-to-diameter aspect ratio.

Although we chose suitable silver components to formulate ink, the conductivity and flexibility can’t meet the requirement of the project. Therefore, we explored some method to improve the properties of silver ink. To achieve higher conductivity, we focus on how to reduce the contact resistance. Even though micro-flakes have relative small contact points when form conductive network, the contact resistance is an important influence factor that can’t be ignored. We designed a simple way to modify the contact which can make it easier to sinter silver flakes together. After many attempts, we firstly introduced the Ag$_2$O nanoparticles to decorate the surface of silver flakes by precipitation method. These nanoparticles serve as bridge to link different flakes together and
is easily decomposed to Ag at 150°C, which further transfer the physical contact to ohmic contact and benefits to the formation of a continuous conductive network.

Then, we synthesized our silver ink and formed silver electrodes by blade-coating. A series of characterization such as SEM, TEM, resistivity measurement, flexibility measurement, etc. were done to explain and analyze our ink system in detail.

Finally, we explored to print our silver inks on curved surface by 3D printer and optimize the parameters of printing process. In next section, I will introduce our project’s progress in detail from silver ink formulation to silver electrode’s formation and characterization.

2. Silver Ink Formulation and Characterization

2.1 Synthesis of Silver Nanowires and Characterization

2.1.1 Growth Mechanism

We use the most popular method polyol synthesis to synthesize silver nanowires. It was firstly put forward by Xia et al.,[40] which includes reduction of silver nitrate by ethylene glycol (EG) in the presence of polyvinyl pyrrolidone (PVP) as a capping reagent. At elevated temperatures, EG undergoes self-oxidation and forms acetaldehyde, which serves as reductant to reduce silver ions, as shown in follow equation:

\[
\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}
\]

\[
2\text{Ag}^+ +2\text{CH}_3\text{CHO} \rightarrow 2\text{Ag}^0 + \text{CH}_3\text{COCOCH}_3 +2\text{H}^+
\]

Initially, most of the reduced silver atoms form decahedral seeds with \{111\} facets on all of their surfaces, which are considered to be the most stable nuclei. Then, since \{100\} surfaces will be capped and passivated by PVP molecules through the interaction with oxygen or nitrogen of
pyrrolidone units, silver atoms tend to aggregate at twin boundaries at the ends of nanowires, resulting in uniaxial growth of silver nanoparticles to nanorods, as shown in Fig. 7.

2.1.2 Experiment

Raw materials: Polyvinyl pyrrolidone (PVP) (MW=55K and 360K), ethylene glycol, ferric chloride (FeCl$_3$) and silver nitrate (AgNO$_3$) were offered by Sigma-Aldrich.

Initially, 50 mg PVP (MW=55K), 100 mg PVP (MW=360K) were added into 15mL EG, then the solution was stirred overnight to guarantee fully dissolution. Next, 150mg AgNO$_3$ was added into the solution. After fully dissolved, 2.8g FeCl$_3$ (600mM in EG) solution was injected by a pipet and mixed for about 1 min. Then, the mixture was transferred into a round-bottom flask reheated to 130℃. The temperature was kept for another 150 min with stirring for first 30min. When the reaction was finished, the product was washed by IPA and water three time through centrifuge and then re-dispersed in IPA to produce a final dispersion.

Figure 7. Schematic illustration of the Ag NWs growth mechanism. Reproduced with permission from [ref. 40].
2.1.3 Characterization of Silver Nanowires

The silver nanowires were characterized by SEM, as shown in Fig. 8. Those nanowires had a diameter and length around 70 nm and 15 μm. Almost all the silver nanoparticles were removed after washing, and the diameter of silver nanowires rose a small amount in a larger scale synthesis. According to these images, we also find that there are a few silver nanowires with some angles as shown in Fig. 8(c) and (d). However, no literature has reported the silver nanowires with this shape, the formation process of these special Ag nanowires relates to the change of growth direction. More detailed explanation need further research. Besides, the percent of these curved silver nanowires is really small. How to increase the percent is another important task for our project.

Figure 8. SEM images of Ag nanowires (red zone: Ag NWs with angles)
2.2 Decoration of Silver Flakes with Silver Oxide Nanoparticles

According to our discussion about conductivity, the contact resistance contributes to the resistivity of silver micro-flakes inks mostly, which requires us to reduce the contact resistance. We can consider it from two aspects. One is decreasing the number of contact. The other is to improve the quality of contact that change physical contact to ohmic contact. In our experiment, we choice silver micro-flakes as main conductive component which has less contact surface than silver nanoparticles when form silver electrode. For improving the quality of contact interface, in the beginning, we want to decorated silver flakes with Ag nanoparticles. However, as we all know, all Ag nanoparticles have surfactant on their surface that prevent aggregation. The surfactant is hard to be removed at low temperature and influence the conductivity largely. On the other hand, it is basically impossible to deposit silver nanoparticles on the flakes’ surface directly, which require a two-step procedure that increase the complexity of our method and is hard to apply in industry. Therefore, we explored Ag$_2$O nanoparticles as a substitute of Ag nanoparticles. There are some advantages for Ag$_2$O nanoparticles decoration. First, there is a convenient and easy way to directly deposit Ag$_2$O nanoparticles on the surface of silver flakes without any surfactant. Second, Ag$_2$O is not stable, and it is easier to be decomposed to Ag at low temperature which will not affect our final conductive network.

2.2.1 Growth Mechanism

We proposed a simple precipitation method to synthesize Ag$_2$O nanoparticles to decorated the surface of silver flakes. The growth mechanism of the Ag$_2$O nanoparticles can be clarified by the chemical reactions and crystal growth behaviors of silver oxides.$^{[41]}$ During the reaction system, the NaOH serves as source of hydroxyl ions to control the pH value of solution. The silver ions
react with OH- ions to form AgOH, which dissociates to form Ag₂O nuclei, according to the following reactions:

\[
\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-
\]

\[
\text{AgNO}_3 \rightarrow \text{Ag}^+ + \text{NO}_3^-
\]

\[
2\text{Ag}^+ + 2\text{OH}^- \rightarrow 2\text{AgOH} \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}
\]

2.2.2 Experiment

Raw materials: Silver nitrate (AgNO₃) was obtained from Sigma-Aldrich. Silver flakes (EA-3106) were purchased from Metalor. Ethanol was supplied by Decon Labs. Sodium hydroxide was gained from Fisher Scientific.

First, 0.0849g silver nitrate (AgNO₃) was dissolved in 140 ml ethanol solution. Then, 1g silver flakes was dispersed into the solution, followed by sonicating for 30min to guarantee good dispersion of silver flakes. Next, the solution was removed to the stir plate with stir speed at 450 rpm. 1ml 0.5 mol/L NaOH ethanol solution was drop by drop into above solution. When the whole solution system was mixed uniformly, adjust the stir speed at 300 rpm. After 15 hours, the product was washed by mixture of ethanol and water three times, and then dried at 60 °C. The as-synthesized products were prepared to be characterized in term of their morphology and structure and applied to silver ink formulation.
2.2.3 Results and Discussion

**Figure 9.** SEM images of silver flakes from (a) pure silver flake and (b)-(d) decorated silver flakes

From **Fig. 9**(a), we can see that the size range of pure silver flakes is 10 μm-20 μm. **Fig. 9**(b)-(d) shows that there are some nanoparticles distributed on the surface of silver flakes, which is the evidence that some nanoparticles have been successfully decorated on pure silver flakes. On the other hand, no obvious nanoparticles are out of flakes, which means most nanoparticles are coated on the surface with no waste. For further characterize Ag\textsubscript{2}O nanoparticles, TEM was used to measure the nanoparticles’ size and crystal structure. From **Fig. 10**(a), we can see that black area represents silver flake because it is so thick that hard to be penetrated by electrons. In contrast, small nanoparticles can be obviously observed on the silver flakes’ surface. And these nanoparticles are about 20 nm.
Figure 10. TEM images of Ag$_2$O nanoparticles decorated on silver flakes (a) (b) before and (c) (d) after annealing

Additionally, Fig. 10(b) shows that the interlayer spacing of these nanoparticles is 0.2361nm, which corresponds to the plane (200) of Ag$_2$O. Based on these images, we make sure that Ag$_2$O nanoparticles have been successfully deposited on the surface of silver flakes. Except for verifying the decoration, we also proved the stability of Ag$_2$O nanoparticles. According to our expectation, we hope that Ag$_2$O nanoparticles can be decomposed at relative low temperature to satisfy flexible electronics application. Therefore, we measure the change with TEM after annealing this sample at 150°C for 30min. Fig. 10(c) elucidates that two different Ag$_2$O nanoparticles on different flakes are sintered together to form a bridge linking two different silver flakes. At high resolution images,
from the interlayer spacing value, it is evident that Ag₂O nanoparticles has been transferred to Ag, which illustrates that at 150°C, it is enough to decompose Ag₂O nanoparticles and sinter them together to modify the interface between different flakes and form a continuous conductive network.

2.3 Silver Ink Formulation and Film characterization

2.3.1 Silver Ink and Electrode Formulation

Raw material: (Di)propylene glycol methyl ether and ethyl cellulose were obtained from Sigma-Aldrich.

We chose a common solvent (di)propylene glycol methyl ether and ethyl cellulose as our silver ink’s solvent and binder, respectively. The weight percent of silver component was controlled at 70%.

First, ethyl cellulose was added to dipropylene glycol methyl ether at the weight ratio of 1:4, and stirred for 6 h to make the solution. After that, silver flakes with different forms (silver flakes, silver flakes decorated with Ag₂O nanoparticles and silver nanowires) and the vehicle were mixed at the weight ratio of 7:3. Using THICKY mixer at 1700 rpm for 15 min to gain the final silver ink.

Next, using blade coating to fabricate silver electrodes. The substrate (PET) was fixed by two pieces of tapes, then suitable amount of silver ink was deposited on the range of top areas, and a thin film formed by scraping of the blade on the tape. Finally, when all the solvent evaporated, a think film of silver was obtained. All samples were annealing at 150°C on hot plate after coating.
2.3.2 Electrical Resistivity of Silver Electrodes

Electrical resistivity is defined as follows:

$$\rho = \frac{R \cdot A}{L}$$

where $\rho$ is the resistivity ($\mu\Omega\cdot m$, or $\Omega\cdot m$), $R$ is the measured resistance of a conductor, $A$ is its cross-sectional area, and $L$ is the film length.

The most common method to test electrical resistivity is using sheet resistance that can be directly measured by a four-probe based instrument to calculate the resistivity. First, the sheet resistance ($R_s$) of silver thin film was measured by a sourcemeter (Keithley 2450, Tektronix) with a four-point probe setup. Next, the thickness of thin film was obtained by profilometer (Dektak XLT-Bruker). Finally, the resistivity of thin film can be calculated as follows:

$$\text{Resistivity} = R_s \cdot \text{Thickness}$$

First, we measure the influence of Ag$_2$O nanoparticles decoration on the resistivity value. The resistivity of silver electrodes with different decoration ratio was shown in Fig. 11. It demonstrated that the lowest resistivity can be acquired when the Ag$_2$O nanoparticles and silver flakes at the weight ratio of 1:9. And the lowest resistivity of silver electrode was $1.5 \times 10^{-5} \Omega \cdot \text{cm}$, which reduced by 35% compared with non-decoration silver electrode. Moreover, if we increased the weight percent of Ag$_2$O nanoparticles, the resistivity would increase.
Figure 11. Resistivity of silver films with (a) different weight content of Ag\(_2\)O; (b) different weight content of AgNWs

For explain this trend, we characterized the morphology of silver electrodes with different weight percent of Ag\(_2\)O nanoparticles. The cross-section of silver electrodes was shown in Fig. 12. It showed that with Ag\(_2\)O nanoparticles increasing, silver flakes tend to aggregated which lead to non-uniform conductive network formation due to high specific surface area because aggregation can reduce the surface area that reduce the surface energy. Furthermore, this tendency can be avoided by increasing the amount of solvent. However, it means that we lost the compactness of our final film. As we discussed before, the loading density of silver component plays a significant role in conductivity. On the other hand, the function of Ag\(_2\)O nanoparticles is just modifying the contact between silver flakes, we need to find the suitable amount of deposition. The weight percent of silver components in all silver inks that we formulated was kept at 70%. Hence, it is
more and more hard to make uniform ink as the weight percent of Ag$_2$O nanoparticles increases. In other words, non-uniform silver ink is difficult to make high quality thin film, let alone high conductivity.

**Figure 12.** The cross-section of silver electrodes (a)(d): pure silver flakes; (b)(e) 10% Ag$_2$O nanoparticles decorated silver flakes; (c)(f) 20% Ag$_2$O nanoparticles decorated silver flakes
For explaining the reduction of resistivity after 10% Ag₂O nanoparticle decoration of silver flakes, we also measure the normal view of pure silver flake inks (Electrode 1) and 10% decorated silver flakes ink (Electrode 2), as shown in Fig. 13. At the same resolution, the number of flakes in the non-decorated silver flakes ink was more than decorated silver flakes ink because the outlines of most silver flakes in Electrode 2 weren’t obvious, which means these silver flakes were sintered together and no obvious interface. Compared with Electrode 2, Electrode 1 don’t have this feature, most flakes were separated and the contact between flakes isn’t clear.

![SEM images of silver electrodes: (a) (c): pure silver flakes; (b) (d): decorated silver flakes](image)

**Figure 13.** SEM images of silver electrodes: (a) (c): pure silver flakes; (b) (d): decorated silver flakes
To further characterize the interface between different silver flakes, we measure these electrodes at ultra-high-resolution mode in SEM. As shown in Fig. 14, the flakes in Electrode 1 were linked by polymers and no direct contact. However, in Electrode 2, the Ag$_2$O nanoparticles served as bridge to link flakes together which improve the quality of interface largely. As we all known, the contact resistance has a great influence on the conductivity of silver electrodes. After decoration of silver flakes, due to the change of contact, the conductivity will increase.

![High resolution SEM images of silver electrodes](image)

**Figure 14.** High resolution SEM images of silver electrodes: (a) (b): pure silver flakes; (c) (d): decorated silver flakes
**Figure 15.** The mechanism of silver oxide decoration for silver electrodes

**Fig. 15** illustrated the mechanism of Ag$_2$O decoration for silver electrodes. As shown in **Fig. 15**(a), for pure silver flake, the contact of flakes was mostly physical contact, which has much high resistance. After we deposited Ag$_2$O nanoparticles on the surface of flakes, after annealing, these nanoparticles can be decomposed to silver and sintered to connect different silver flakes together that change the physical contact to ohmic contact. Therefore, the decoration of silver flakes with Ag$_2$O nanoparticles can reduce the resistivity of silver electrodes.

Next, we also compared the density and roughness of silver electrodes. High density means low porosity that lead to high conductivity. As shown in **Fig. 16**, after decoration, the density of silver electrode had increased by 8.2% compared with pure silver flake. Thus, Ag$_2$O decoration can help us gain more compact silver film which also corresponds to SEM image and resistivity data. In addition, from the roughness measurement, it demonstrated both roughness is below 1 µm. The roughness of decorated silver electrode is a little higher than pure silver electrode, which was attributed to the Ag$_2$O nanoparticles, as shown in **Fig. 17**. Although low roughness is our expectation, the larger roughness didn’t influence the conductivity values. Therefore, the roughness factor is small and can be neglected in our experiment.
Figure 16. The density of different silver electrodes

Figure 17. Roughness of different silver electrodes
In addition, we also measured the influence of adding silver nanowires on resistivity. We replaced some decorated silver flakes with silver nanowires at weight percent of 1% and 2% in whole ink, respectively. Due to the high specific surface ratio, even a little Ag NWs can change the properties such as viscosity and homogeneity of our silver ink, which impact the quality of silver films. Fig. 18 demonstrated the variation trend of resistivity. When the weight percent of Ag NWs kept at 1%, the change of resistivity was statistically insignificant that can be ignored. However, when we increased the weight percent of Ag NWs continuously, we found that the resistivity increased and the effect should be considered. On the other hand, to obtain good flexibility, the existence of Ag NWs is necessary. Therefore, optimizing the amount of Ag NWs to balance the conductivity and flexibility is a significant step.

**Figure 18.** The resistivity of silver electrodes with different weight content of AgNWs
2.3.3 Flexibility Measurement

**Figure 19.** Optical images of a silver electrode in (a) flat state with initial length $L_0$; (b) (c) bent states with length of $L$; (d) the maximum bend radii

We conducted bending-resistance tests to investigate the mechanical flexibility and stability of silver electrodes. The method that we used to measure resistance at different bend state was shown in Fig. 19. First, traces with length of 6 cm and 9 cm and width of 5 mm were fabricated on PET substrate by blade-coating. Then, the resistivity of two electrodes were measured at flat state. Next, we bent these electrodes at different bend rate and measure corresponding resistivity value. **Fig. 19**(a) shows the initial length of electrode is $L_0$. After bend, the actual distance $L$ was shown in **Fig. 19**(b) and (c). We calculated the distance difference $L_0 - L$, then divide the value by the initial
distance \( L_0 \) to calculate the bend rate of the electrode. The maximum bend rate is 100\% that was shown in Fig. 19(d) when \( L \) becomes zero. Moreover, strain and compression have different effects on the conductivity, therefore we also bent silver electrodes at opposite direction to measure the change of resistivity when electrodes were strained or compressed.

![Graphs showing resistance change](image)

**Figure 20.** The change of electrical resistance in different electrodes with (a) \( L_0 = 6 \, \text{cm} \) and (b) \( L_0 = 9 \, \text{cm} \) as a function of bend rate; (c) \( L_0 = 6 \, \text{cm} \) and (d) \( L_0 = 9 \, \text{cm} \) as a function of bend cycles (bend rate = 100\%) (strain state)

Fig. 20(a) and (b) presented the relationship between bend rate and resistance change when electrodes were strained, corresponding to \( L_0 = 6 \, \text{cm} \) and \( 9 \, \text{cm} \), respectively. We chose AG-510
silver conductive ink that provided by Applied Ink Solutions as our reference sample. We measured five samples fabricated using different silver inks. They were AG-510, pure silver flakes ink, decorated silver flakes ink, decorated silver flakes with 1% Ag NWs ink and decorated silver flakes with 2% Ag NWs ink, respectively. From the two groups data, pure silver flakes ink owned the worst flexibility. No matter what initial length is, it exhibited the largest resistance increasing rate. After decoration, there is an obvious improvement of flexibility. However, the resistance increasing rate was also higher than AG-510 silver ink. After adding Ag NWs to silver ink, the flexibility was enhanced again, that was close to our reference sample. The loss of conductivity is mainly attributed to the cracks and separation of silver flakes. According to our discussion before, the decoration of silver flakes improves the contact of flakes that not only improve the conductivity but also increase the crack resistance. On the other hand, Ag NWs have excellent mechanical compliancy due to the large length-to-diameter aspect ratio, which is beneficial to flexible electronics application. Therefore, combining these two aspects are conductive to the flexibility.

In addition, bending durability is another important consideration for flexible electronics. Hence, we investigated electrical resistance change of different electrodes as a function of the number of bend cycles with the bend rate is 100%. Fig. 20(c) and (d) corresponded to the initial length \( L_0 = 6 \, \text{cm}, 9 \, \text{cm} \), respectively. As we expected, pure silver flakes ink that has lowest flexibility also owned lowest bending durability. Its resistivity changed a lot after 50 cycles which results from the poor contact between flakes. Although the combination of decoration with Ag\(_2\)O and Ag NWs is also good for bending durability, the bending durability of silver flakes/nanowires ink is lower than that of AG-510 silver ink.
Figure 21. The change of electrical resistance in different electrodes with (a) \( L_0 = 6 \, \text{cm} \) and (b) \( L_0 = 9 \, \text{cm} \) as a function of bend rate; (c) \( L_0 = 6 \, \text{cm} \) and (d) \( L_0 = 9 \, \text{cm} \) as a function of bend cycles (bend rate = 100%) (compressive state).

When silver electrodes were compressed, the relationship between bend rate and resistance change is different. As shown in Fig. 21(a) and (b). Except for AG-510, the resistivity change of other silver inks was very small, which can be ignored. However, it is interesting for us that the resistivity of AG-510 silver ink reduced as bend rate increased, which was opposite to the result when it was in strain state.
For bending durability in compressive state, Fig. 21(c) and (d) told us that besides AG-510, after 50 bend cycles, the resistivity of other silver ink increased a little. No matter what initial length was, the maximum resistivity change happened in pure silver flake ink, which meant that Ag\textsubscript{2}O decoration and Ag NWs is also beneficial to the bending durability in compressive state. However, as bend cycles increased, the resistivity of AG-510 ink reduced which is also opposite to strain state.

For possible reason of AG-510 silver ink owns excellent bending durability and good flexibility in compressive state, we proposed that it is attributed to the polymer matrix structure that formed in silver electrode. Because fine polymer matrix can endure high bend cycles that reduce the possibility of crack formation. Compared with our simple vehicle, AG-510 has more complicated and advanced recipe for their silver ink. Therefore, if we want to further improve the flexibility, optimizing our ink’s recipe is our main work.

3. 3D Printing Process

3.1 3D Printer Description

As we discussed in Section 1.3.4, micro-dispensing printing can be used for 3D printing. In this work, we used an nScrypt-3Dn-300 for printing, as shown in Fig. 22. This printer is capable of scanning irregular surfaces and dispensing different inks onto that surface. A vacuum chuck is equipped to hold substrates securely in place and to keep flexible substrates flat. This printer also has sensors and cameras for alignments, scanning the shape of a surface, and recording the printing process. The nScrypt-3Dn-300 can print over 600 mm×600 mm area and achieve feature sizes below 50 µm using SmartPump\textsuperscript{TM} technology.
3.2 Printing Process

We choose watch-glass as our substrate and tape the surface with Kapton which can be detected by laser and can be easily wetted by silver inks. First, we generated a DXF file containing the CAD drawing of the desired print and convert it to a print path script file which contains the move commands by suing nScrypt’s PCAD software. Then, we assembled SmartPump with valve rod and valve body where we installed a pen tip. Next, we loaded our silver flake/nanowire composites inks into a 3cc syringe that is then screwed into the SmartPump and attach the pressure adapter (pressure line) to the end of the syringe. The diameter of the tip is 125 µm which should be 10 to 20 times larger than the maximum flake size to avoid clogging.
When a back pressure is applied to the syringe that holds the ink, the inks are dispensed. Then the inks run through the valve of the SmartPump and out of the pen tip in a controlled fashion. Therefore, a good quality dispensing depends on the fine tuning of opening and closed positions for the SmartPump, which is customized for every specific ink viscosity and back pressure used. The printing process is controlled by the printing speed and the clearance (height above the substrate). Therefore, the combination of dispensing process and printing process determines the quality of final print pattern.

Initially, we opened the pressure and fine good “closed” and “open” positions for that specific pressure. A good “closed” position is where the ink is not flowing, but about to come out of the tip. And a good “open” position is on that allows for a steady, uniform flow of ink from the tip. Then in the printing job window, we choose our script and adjust the printing speed, valve opening and opening speed, and waiting time before movement starts. Next, in laser scan window, we set the scan speed, resolution, and area. After that, we start the whole printing process. The printer scanned the curved surface of substrates firstly. Then, a printing process run following our set parameter. Finally, we obtained the final silver electrodes on curved surface.

3.3 Printing Results discussion

Based on above description, we know that a good quality silver electrode is related to the combination of the variables with the speed and the clearance used for printing. There are four important parameters for printing process: valve opening, pressure, printing speed and clearance. Pressure need to be enough large to dispense the silver ink to the valve and depends on the viscosity of inks. High viscosity need high pressure. Valve opening directly influence the flow of silver ink. Appropriate valve opening helps to gain a steady and uniform flow. For printing speed, high speed cannot form continue silver line because the ink is not enough for printing. Moreover, if the tip is
not close enough to the substrate, the ink will not adhere to the surface during printing and form globs attached to the sides of the tip. Therefore, if we want to obtain a good printed pattern of silver inks, we need to adjust these parameters to optimize the final product.

After an iterative process of parameter adjustment, we optimized the process and get the optimal printing parameters for our silver ink. Table 2 shows the parameters that we optimized in printing process for our silver inks.

**Table 2.** The parameters for 3D printing process

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>25-30 psi</td>
</tr>
<tr>
<td>Valve opening</td>
<td>0.06 mm</td>
</tr>
<tr>
<td>Printing speed</td>
<td>5 mm/s</td>
</tr>
<tr>
<td>Clearance</td>
<td>0.05 mm</td>
</tr>
</tbody>
</table>

![Figure 23. The photo of silver electrodes on curved surface.](image)
From Fig. 23, we can see that silver electrodes with zig-zag pattern were printed successfully on the curved surface. We used profilometry to characterize these patterns. And we found that the thickness of electrodes is uniform and about 10 µm. The width of each line is a little non-uniform because the width of the part near the corner was a litter larger than that of middle part. The variation was about 80 µm and the average of width was about 300 µm.

4. Conclusions

In this report, we explored the formulation and 3D printing process of higher conductive silver flake/nanowire ink and characterized the conductivity and flexibility of our silver electrodes. From above discussion, we have come to following conclusion:

(1) The decoration of silver flakes with Ag₂O nanoparticles can improve the contact between flakes effectively and make silver electrode more compact, which increase the conductivity obviously. When the weight ratio of Ag₂O nanoparticles to silver flakes reaches 1:9, the conductivity reduced by 35%;

(2) The existence of Ag NWs to silver ink impact the conductivity weakly when we add suitable amount Ag NWs to our silver ink. When the weight percent of Ag NWs is 1%, there is no obviously change in conductivity;

(3) For flexibility, Both the decoration of silver flakes with Ag₂O nanoparticles and adding Ag NWs are useful methods to improve the bend resistance and durability of our silver electrodes.

(4) For 3D printing process, the optimal parameters for printing were obtained and silver inks had been successfully printed on curved surface.
So far, we have synthesized the highly conductive and flexible silver flakes/nanowires ink and the lowest resistivity that we achieved is about $1 \times 10^{-5} \ \Omega \cdot \text{cm}$ after annealing $150 \ ^\circ\text{C}$ for 1 hour that is very close to the aim of resistivity on the order of $10^{-6}$. And the Demo of printed silver electrodes on curved surface were obtained by 3D printer.

However, there are some aspects need to be improved:

(1) According to the bend test results, compared with commercial silver ink, the flexibility of our silver ink can be further improved. We can resolve it form two methods. One is to balance the high conductivity and good flexibility and optimize the amount and quality of Ag NWs. We find that Ag NWs plays a significant role in flexibility. If we can increase the amount of Ag NWs, the flexibility can be better. On the other hand, our group also try to synthesize more thinner and longer Ag NWs which have better mechanical compliancy. The other method is concentrating on the polymer system. As we mentioned before, the polymer matrix is also important to resist bend force. Now, in our silver ink, we use the simplest polymer system that only contains solvent and binder. If we choose suitable additive such as dispersion agent, surfactant, antifoaming agent to optimize silver flake/nanowires ink recipe, it also contributes to the improvement of flexibility such like commercial silver inks.

(2) The process of printing silver electrodes on the curved surface by nScrypt-300-3dn 3D printer need to be further optimized. From current analysis of the patterns, the width of the lines isn’t uniform. How to get more uniform and higher resolution printed pattern is our next main focus.
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