Synthesis of silver nanowires for highly transparent conductive films and electrochemical reduction of carbon dioxide

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Thesis Title

Synthesis of silver nanowires for highly transparent conductive films and electrochemical reduction of carbon dioxide

Thesis Abstract

The traditional indium tin oxide (ITO)-based transparent conductive films and electrodes have been widely applied in many fields and used in various electronics in the past decades. However, its brittle property and costly manufacturing process limit the development of ITO for next-generation electronic devices, which need the features of light weight, flexibility, and low cost. Silver nanowires (AgNWs) have attracted considerable attention from researchers among many candidates due to their outstanding electrical, mechanical, and optical properties. Many synthesis methods of AgNWs have been demonstrated recently, but there are still some parameters that are unclear and need further investigations.

In this thesis, one-step solvothermal synthesis of AgNWs has been studied and explored. AgNWs with a high aspect ratio (~2000) were successfully obtained by using this method. The morphology of AgNWs was significantly affected when tuning the different factors, including the heating temperature of PVP dissolution, the molar ratio of PVP/AgNO3, the molecular rate of PVP, and the concentration of ionic assistants. Moreover, another latest modified polyol method, the Maillard reaction process, has also been introduced and researched in this thesis. The ultra-long AgNWs (~100 μm) were successfully generated through the Millard reaction method using ammonium chloride and glucose as reacting agents of Maillard reaction products (MRPs). Effects of experimental parameters such as reaction time and pressure environment on the morphology of AgNWs have also been investigated. Besides, the extra salt additive (NaBr) was employed to see whether the NW diameter would become thinner to achieve the high aspect ratio AgNWs. The NW diameter was greatly reduced when the molar ratio of NH4Cl/ NaBr was at 40:1; however, a large amount of Ag nanoparticles were generated, which could significantly affect the overall performance of AgNWs.

The AgNWs-based transparent conductive films (TCFs) were fabricated in this project. With the help of annealing post-treatment, TCFs with low sheet resistance (~22 Ω/sq) and high transmittance (86 %) were prepared using the high aspect ratio AgNWs. In addition, the AgNWs were applied to the electrochemical reduction of CO2 to syngas and showed the potential of syngas production. Nevertheless, more factors and studies need to be carried out to improve the Faradic efficiency of syngas production. This study indicates that ultra-thin and long AgNWs can serve as the replacement of ITO, which also reports its potential performance in the electrochemical reduction of CO_2

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Abstract

The traditional indium tin oxide (ITO)-based transparent conductive films and electrodes have been widely applied in many fields and used in various electronics in the past decades. However, its brittle property and costly manufacturing process limit the development of ITO for next-generation electronic devices, which need the features of light weight, flexibility, and low cost. Silver nanowires (AgNWs) have attracted considerable attention from researchers among many candidates due to their outstanding electrical, mechanical, and optical properties. Many synthesis methods of AgNWs have been demonstrated recently, but there are still some parameters that are unclear and need further investigations.

In this thesis, one-step solvothermal synthesis of AgNWs has been studied and explored. AgNWs with a high aspect ratio (~2000) were successfully obtained by using this method. The morphology of AgNWs was significantly affected when tuning the different factors, including the heating temperature of PVP dissolution, the molar ratio of PVP/$AgNO_3$, the molecular rate of PVP, and the concentration of ionic assistants. Moreover, another latest modified polyol method, the Maillard reaction process, has also been introduced and researched in this thesis. The ultra-long AgNWs (~100 μm) were successfully generated through the Millard reaction method using ammonium chloride and glucose as reacting agents of Maillard reaction products (MRPs). Effects of experimental parameters such as reaction time and pressure environment on the morphology of AgNWs have also been investigated. Besides, the extra salt additive (NaBr) was employed to see whether the NW diameter would become thinner to achieve the high aspect ratio AgNWs. The NW diameter was greatly reduced when the molar ratio of NH_4Cl/ NaBr was at 40:1; however,

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List of abbreviations

Abbreviation	Definition
AIN	Aluminum Nitride
AR	Aspect ratio
CNT	Carbon nanotube
CO	carbon oxide
CO_2	carbon dioxide
DFT	Density functional theory
DI	Deionized water
EE	Energy efficiency
EG	Ethylene glycol
EHD	Electro hydrodynamic jet
ETD	electron trap distributions
FE	Faradic efficiency
H_2	Hydrogen
H_2O	Dihydrogen monoxide
HER	Hydrogen evolution reaction
ITO	Indium tin oxide
KBr	Potassium bromide
$KHCO_3$	Potassium hydrogen carbonate
MPRs	Maillard reaction products
MW	Molecular weight
$AgNO_3$	Silver nitrate

AgNWs	Silver nanowires
NW	Nanowire
NWs	Nanowires
EtOH	Ethanol
OLED	Organic light-emitting diode
PDMS	Polydimethylsiloxane
PET	Polyethylene terephthalate
PVP	Polyvinylpyrrolidone
RHE	Reversible hydrogen electrodes
RR	Reduction reaction
SEM	Scanning electron microscope
TBAB	Tetrabutylammonium bromide
TCFs	Transparent conductive films
TEM	Transmission electron microscope
UT	Ultra-thin
UV	Ultraviolet
XRD	X-ray crystallography

1. Introduction

1.1 Background

Nowadays, there is an increasing demand for electronic devices such as smartphones, smartwatches, OLED displays, heaters, and sensors, which have revolutionarily changed our daily lives. These smart devices connect with the internet, collect and exchange massive data in a short period, and immediately respond to the information to us, making life easier and more convenient. Therefore, it is hard to go out without any electronic devices today, and they are now becoming an important or even a necessary part of human being's life.

Transparent conductive electrode is a crucial component of various electronic devices. Indium-doped Tin Oxide (ITO) is a commercially dominant transparent conductor in electronic devices on account of its excellent optical transparency and low sheet resistance. With the development of technology, the trend of technology for the future of electronics needs light and low-cost smart devices in wearable, flexible and transparent forms that can be adhered to clothes and human bodies. However, the high cost and scarcity of indium have posed serious challenges to its further electronic applications. In addition, it is hard for ITO to maintain the structure and integrity under mechanical stress as it is rigid and easy to crack through bending and stretching. From this, ITO might not be a suitable option for flexible transparent electrodes, and therefore flexible materials with similar characteristics to ITO are highly needed. Recently, a variety of conductive materials, including carbon nanotubes, conductive polymer, graphene, MXene, and silver

nanowires (AgNWs), have been carried out for potential applications in flexible transparent electrodes. Due to the excellent flexibility, electrical conductivity, and high transparency, AgNWs have now been taken consideration as a promising material for the ITO's replacement. They can be used for flexible applications, including foldable smartphones, curved displays, and wearable devices[2].

Over the last several years, many synthesis methods of AgNWs have been carried out, including template method, polyol method, and hydrothermal method. The polyol process has been the universal way to prepare AgNWs with uniform morphology among these approaches [3]. Although the polyol reduction process can easily synthesize AgNWs with diameters of 30 – 50 nm and aspect ratio (length to diameter) of around 1000, there are still some drawbacks associated with the method to be studied. For example, during the synthesis process, various factors, including stirring speed, salt concentration, temperature, and reaction time will greatly influence the form of AgNWs, and thus the experimental parameters need to be carefully controlled. Theoretical and experimental investigations have indicated that thin and high aspect ratio AgNWs can have better overall performance in conductivity and optical transmittance. Enhancing the performance of AgNWs and finding the simple producing way or post-treatment on AgNWs networks to overcome the above limitations have attracted intense interest due to the emerging need for transparent conductive smart devices. Although some factors are still unclear, it is believed that a better aspect ratio AgNWs can be produced through further experiments and analysis.

This project aims to explore the better aspect ratio (length to diameter >2000) of AgNWs with different methods and investigate their electrical and optical performance for

transparent conductive electrode applications.

1.2 Scope of research

The content of the thesis focuses on three parts.

Chapter one and the second chapter are in the first part. This part is aiming to introduce the previous studies, background, and knowledge of AgNWs. The research status, the comparison of different synthesis processes, and the various fabrication methods are carried out in the middle of this part. At the end of the first part, the application of AgNWs and their prospects are mentioned.

The second part is a significant part of this thesis, including the chapter three to six. In the third and fourth chapters, the two different synthesis processes (solvothermal process and Maillard reaction process) were used to synthesize the AgNWs sample. To have AgNWs with better performance, the high aspect ratio AgNWs are needed. Therefore, the various formations of silver products under different experimental conditions and parameters through these two methods were discussed in the first two chapters. In the fifth chapter, the transparent conductive films were fabricated with different samples generated from the two synthesis processes. The optical, electrical, and mechanical properties of the TCFs-based AgNWs were indicated at the end of the fifth chapter. In the sixth chapter, the electrochemical-reduction of carbon dioxide using the as-prepared AgNWs based electrodes was carried out and discussed.

In the last part, the results in the previous chapters were concluded. The future perspectives of AgNWs were mentioned at the end of the part.

2. Literature Review

2.1 Synthesis of silver nanowires

Recently one-dimensional and high aspect ratio NWs have got great attention due to their unique mechanical, chemical, and physical properties. Not only silver but also other metals or metalloids such as copper and silicon can be made into nanowires, and these studies were also well-developed[4, 5]. Since AgNWs have great conductivity, flexibility, and transparency, they can be widely applied in stretchable, foldable, and wearable devices, and numerous studies have been conducted in order to synthesize high quality AgNWs for practical applications. However, many methods about the synthesis of AgNWs have some drawbacks, including low yields, low aspect ratio, ununiform products, and irregular morphologies[6, 7]. There are some methods to synthesize AgNWs in recent years. One is hydrothermal growth[8-10], and the other two are Polyol process and solvothermal synthesis.

2.1.1 Polyol process

These three methods to prepare AgNWs are simple and low cost, especially the polyol process is the most common approach to synthesize AgNWs. A research in polyol process uses poly(vinylpyrrolidone) (PVP) as base-solvent and reductant, which leads to the reduction of precursors and change of metal ions into metal particles. Various studies have successfully used silver precursors to synthesize AgNWs, and ethylene glycol (EG) is is employed as reductant and solvent [3, 11]. The first step in this reaction is called seeding process, in which seed particles are formed via nucleation from precursor in EG. After this, Ag atoms finally grow into AgNWs. For instance, $PtCl_2$ in EG solution is a seed

solution, after $PtCl_2$ being reduced by EG solution, Pt atoms will then become Pt nanoparticles. These nanoparticles are used as crystal seeds to promote the reaction of heterogeneous nucleation as well as the growth of the atoms of silver. PVP and silver nitrate would be added into this solution, including Pt nanoparticles afterward. In this solution, EG, silver nitrate, and PVP are used as polyol, salt precursor, and surfactant respectively. Ag atoms generated through the reduction of silver nitrate will get together and react for a while. This reaction would lead to the growth of Ag nuclei and final formation of AgNWs[12, 13]. However, a study researched by Y. Sun et al. claimed that AgNWs could be synthesized without using external seeds such as $PtCl_2$. Ag atoms will become an amount of AgNWs via the self-seeding process[14]. Ag atoms could grow into uniform AgNWs through the self-seeding process with chemical solutions'-controlled rate. The polyol process synthesis of AgNWs has become the most common way because it can enable large-scale synthesis of uniform NWs [15] **(Figure 1)**.

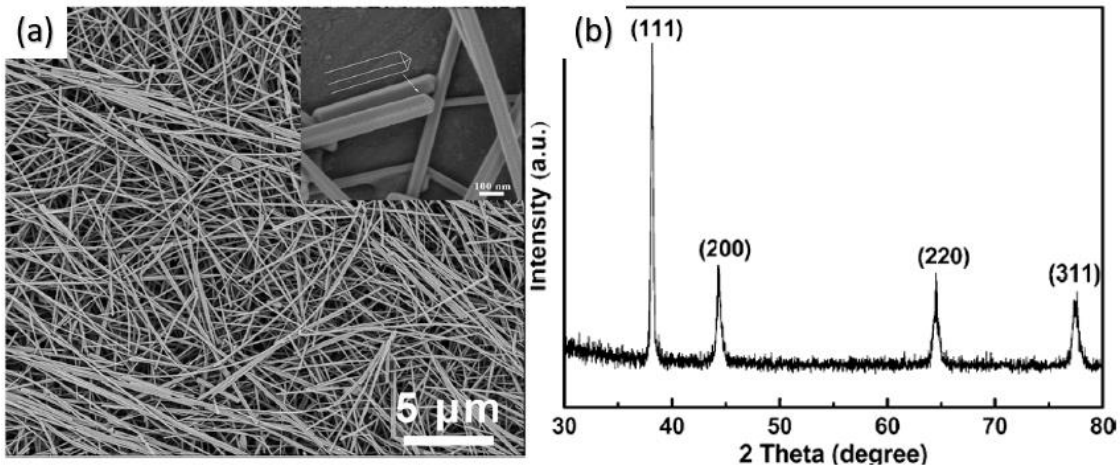

Figure 1 (a) FE-SEM images of uniform AgNWs (b) the XRD images [16]

For example, by the support of PVP and reduction of $AgNO_3$, a large amount of uniform AgNWs with an aspect ratio of ~1000 and a diameter of ~30 nm are produced through the polyol process method with $PtCl_2$. It is believed that the critical points for generating

uniform AgNWs are because that PVP could control the growth rate of silver's structure, and the Pt seed in seed solution can induce silver to grow[11]. For some other examples, Moon et al. successfully synthesized AgNWs whose aspect ratio is around 800, and the length is about 80 – 100 um[17]. An ultrathin AgNWs were demonstrated by Lee, E.J. et al. using the high-pressure polyol synthesis(Section 2.2) [18]. Moreover, Li, B. et al. suggested a method to purify the AgNWs after the polyol process and demonstrated very thin AgNWs with significantly high transmittance[19]. The results of the AgNWs made through the polyol process are in **Table1**.

Table 1 The synthesis of AgNWs through the polyol process

Diameter (nm)	Length (um)	Transmittance (%)	Sheet resistance ($\Omega \boldsymbol{sq^{-1}}$)	Reference
15-30	20	88	40	15
100	80-100	96	100	14
20	40-50	99.1	130	16
30-50	50	N/A	N/A	12
30	50	N/A	N/A	9

2.1.2 Solvothermal synthesis

As mentioned above, there is also a solvothermal synthesis method to produce silver nanowires. Indeed, the polyol reduction process has been the most widespread approach for generating AgNWs over the past several years. Although this polyol process remains substantial advantages, it still has some apparent drawbacks that might affect the final result. Various factors may influence the products, such as the injection pace of chemicals, stirring speed, and chemical injection concentration. From this, the shape and morphology of AgNWs may be influenced, resulting in the bad performance of conductivity and transparency. On the other hand, it is believed that synthesizing AgNWs through solvothermal is much easier and convenient, which can produce AgNWs in one-step synthesis. However, according to the research related to this method recently, it is hard to

synthesize the AgNWs with a thin diameter or long length while in a large aspect ratio. Chen et al.[20] reported a solvothermal process of synthesizing AgNWs, but the quality of the AgNWs does not reach the expectation which their diameter is from 56.6 - 84.2 nm and the aspect ratio ranges from 100 - 500. The AgNWs with the length from 3 – 25 um and the diameter from 80 – 250 nm were demonstrated by Banica et al.[21]. They indicated that these silver nanowires could be obtained using different compositions and ratios of the two solvents. Li et al.[22]successfully used the solvothermal method with dual ionic assistance to synthesize the AgNWs with a diameter of around ~20 nm and ~40um in length, and the 2000 high aspect ratio was achieved.

2.1.3 Purification of silver nanowires

ITO, which is now the most commonly used transparent conductive films or TCFs, has considerably high transmittance with low sheet resistance. Due to this outstanding performance, these TCFs have been applied to various electronic devices, including displays, touch screens, organic light-emitting diodes[23], and solar cells[24]. However, due to the high cost of producing ITO and the coating laggard rates when sputtering, many substitution studies have shown up recently, such as graphene, the conductive polymer[25], carbon nanotube, AgNWs, and other metallic nanowires[26]. In particular, AgNWs are now the most popular promising alternatives to substitute ITO because of their similar properties, including high optical transparency and high conductivity. A study from Li, B., et al. indicates that the increase of AgNWs' aspect ratio will reduce its sheet resistance[27]. This means that AgNWs could have high transmittance with low sheet resistance when they are both in very thin and very long conditions. This performance can reach or even surpass the performance of ITO[19].

In previous studies, some researchers successfully synthesized AgNWs with an ultra-long length of 160um. Although these ultra-long AgNWs could have better performance than the shorter ones, they are too thick to match the performance of ITO[28]. Thus, there is a need for developing a method that can synthesize the AgNWs with both thin diameter (~20 nm) and long length (>50 um) to achieve excellent electrical and optical performance. The most popular method to synthesize AgNWs is the polyol process nowadays, and it can generate a large amount of uniform AgNWs with good quality. However, this method will produce some nanoparticles, which are the by-products of this reaction[29, 30]. Paradel.k.c et al. [31] found that these nanoparticle impurities will influence the conductivity and transmittance of AgNW networks. To avoid this issue, effective methods of purifying these impurities are needed.

In the previous research, Paradel.k.c et al.[31] demonstrated a cross-flow filtration way to clean and purify AgNWs, but this processes was complicated. Accordingly, a more effective purification procedure is required to eliminate the by-products. A simple selective precipitation method was demonstrated by Li, B. et al. [19] to purify the AgNWs. In this process, acetone is added into the synthesized solution to purify the AgNWs. Since AgNWs coated with PVP cannot be dissolved in the acetone solution, AgNWs will agglomerate and precipitate over time. This procedure can be observed visually in which the solution's color will change from light-green to yellow **(Figure 3)**. After purification of AgNWs **(Figure 2)**, AgNWs will then be coated on the glass substrate with spray coating methods, and AgNW films with high optical transparency (~99.1%) can be achieved.

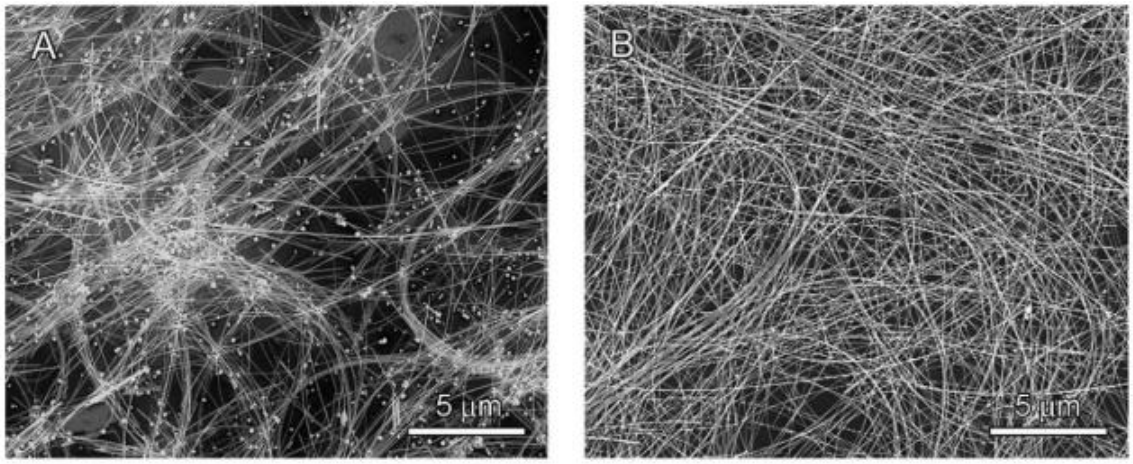

Figure 2 The SEM images of (A) raw AgNWs and (B) purified AgNWs [19]

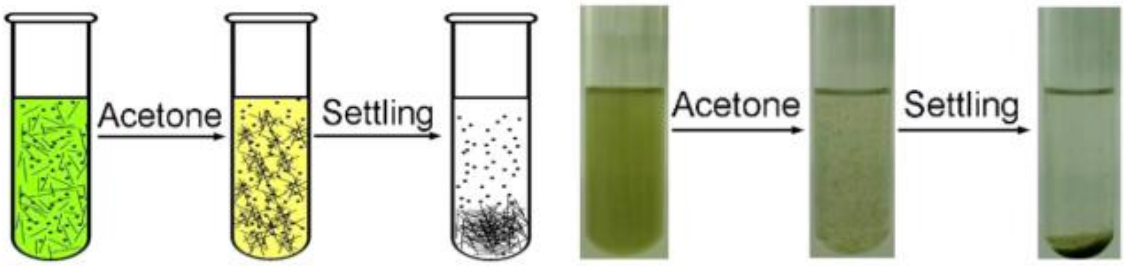

Figure 3 The visual change of the reaction after adding the acetone in the solution containing AgNWs [19]

Figure 4 shows the comparison of transmittance versus sheet resistance between ITO, raw AgNWs and purified AgNWs. Therefore, this purification process is practical to make uniform AgNWs with great quality and the performance of the AgNW transparent electrodes might exceed that of ITO.

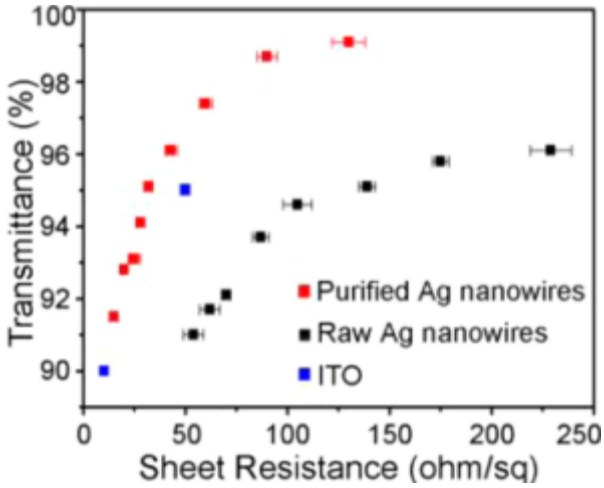

Figure 4 This image shows the transmittance versus sheet resistance for ITO films and AgNWs films after and before purification [19]

2.1.4 Maillard reaction -controlled synthesis

It is known that reduction kinetics is an essential factor of controlling the seeds size and to prepare the nanowires with high aspect ratio. However, the general polyol synthesis of silver nanowires is difficult to adjust the kinetics of reduction during the reaction because the reducing agent is produced from the EG at high temperature, which causes the seeds to grow fast and become bigger. Maillard reaction-controlled synthesis was carried out to limit the size of the seeds and produce the high aspect ratio AgNWs. This method successfully synthesized the CuNWs with the length of 100 um and the average diameters of about 150 nm in the previously published journal article [30], and large-scale transparent flexible films were also fabricated. Nevertheless, there were few studies related to AgNW synthesis with this Maillard-controlled reaction. In 2020, Xiao et al. reported a scalable and straightforward way to synthesize ultra-thin AgNWs with aspect ratio of ~2000 and an average diameter of 18 nm[32]. They used ammonium bromide as an amino compound and glucose as reducing sugar during the reaction. The reaction

between two chemicals produced Maillard reaction products (MPRs). MRPs with strong reducing property can react with $AgNO_3$ at an early stage and low temperature compared to the traditional polyol method. With the assistance of MRPs, Ag-seed was formed at about 100 ℃, and they were uniform in relatively small size. However, this seed of Ag was observed at about 140 ℃ and bigger in diameter in the polyol method, as shown in **Figure 5**. Based on the above results, it is believed that the tiny seed will be created at a low temperature with the help of MPRs in the reaction, which leads to the ultra-thin AgNWs (UT-AgNWs) in the final stage. These UT-AgNWs were successfully used to fabricate TCFs. Because of the thin and the high aspect ratio, it had an outstanding performance in a low sheet resistance around 19 Ω/sq under high transmittance 95%.

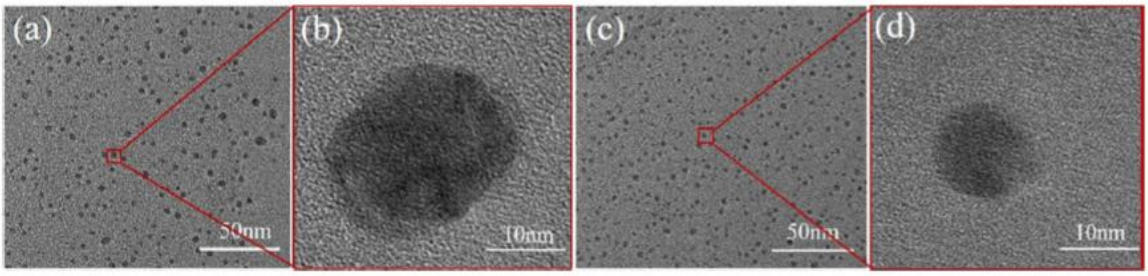

Figure 5 (a, b) TEM images of the seeds produced from polyol method, (c, d) uniform seeds formed from Maillard reaction method [32]

2.2 Factors affecting the synthesis of AgNWs

Many syntheses of AgNWs have been researched for a long time and the methods of producing AgNWs are getting more and more mature. In this section, we will discuss some key factors that affect the morphology of AgNWs during synthesis.

Today, there are various synthesis ways to generate AgNWs via polyol methods. Although these methods are similar, the small changes of some factors, such as temperature,

reaction time, and quantities of reagents, will significantly impact the AgNWs. By changing these factors, we can produce AgNWs with different shapes or sizes.

2.2.1 Temperature

Many studies have found that the temperature could greatly influence the AgNWs because of the temperature-dependent oxidation of ethylene glycol to the reducing agent, glycolaldehyde. In the early stage, most of the synthesis reactions were conducted at 160 ℃, and the reaction time was around 1hr. The lengths of most AgNWs would decrease dramatically when the temperature was above or below 160 ℃[11]. For instance, researchers found no AgNWs were formed in the previous experiments when the temperature was set at 100 ℃[29]. Due to the low temperature, there was no sufficient energy to promote the anisotropic growth of silver nanowires. Simultaneously, if the synthesis temperature were conducted at 185 ℃, the silver nanorods would show up in the end. Xia et al. demonstrated the CuCl-mediated polyol process at 151.5 ℃, and they indicated that the nanowires would change significantly to the nanoparticles when the temperature was conducted 10 ℃ above or below the previous temperature.

It is said that the dimensions of AgNW can have a considerable effect to the performance of AgNWs, especially their optical and conductive properties. From this, there was a research conducted by Wiley et al. [33] and they measured the relationships between temperature and the dimensions change of AgNWs. In this research, they found that the lower temperatures would yield longer AgNWs with larger diameters. Several comparing parameters about the relationship with temperature are given in **Figure 6**.

Additionally, Unalan et al.[34] reported that the diameter of AgNWs would decrease

when the reaction is conducted at a higher temperature. Also, they found that when the synthesis is carried out at 170 ℃, AgNWs will have the highest aspect ratio. Different experimental conditions may lead to these opposite conclusions, and these various findings regarding the temperature may point that the temperature is not the only factor affecting the shapes of the AgNWs. There should be more parameters to affect their morphology.

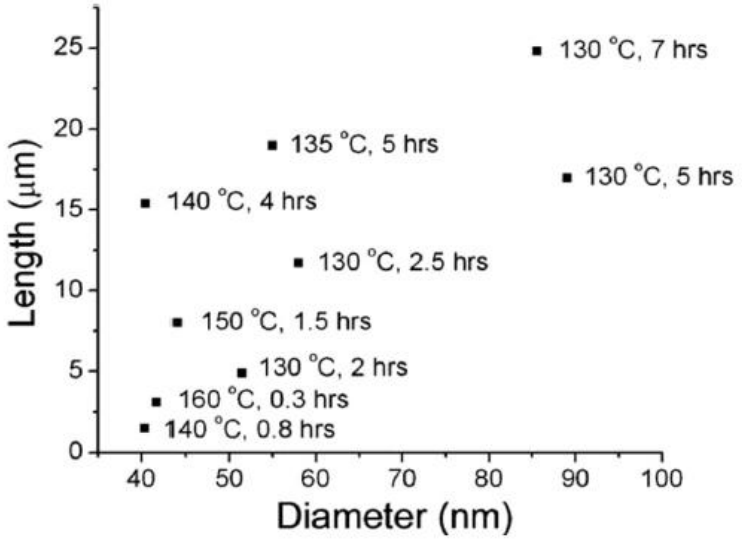

Figure 6 The different conditions of the reaction for generating different lengths and diameters of AgNWs [33]

2.2.2 Exotic species

It is known that exotic species could control and affect the final morphology in the synthesis of AgNWs. Various exotic species have been used to assist the synthesis of AgNWs, such as iron ions, platinum nanoparticles, chloride ions, bromide ions, and glucose. Here, we will talk about how the two most commonly used exotic species, chloride ions, and bromide ions, work to influence the production of AgNWs. In addition, the newly demonstrated Maillard Reaction method with glucose will be introduced to

synthesize AgNWs.

2.2.2.1 The influence of chloride ions

In recent years, many studies have found that chloride ions are crucial in determining the final shapes of silver nanostructure during the synthesis reaction. The lack of or absence of chloride ions will result in irregular shapes in the final product, and the different amounts of chloride ions will have a big impact on the morphology of AgNWs. According to Xia et al.[35], they first found that the chloride ions could prevent the aggregation of silver nuclei which is a primary growth way for nanoparticles. It is said that the chloride ions can stabilize the silver cation and reduce the concentration of silver nuclei by forming the silver chloride (AgCl). Thus, the presence of chloride ions in the reaction could promote the growth of AgNWs. In the early stage, without the assistance of chloride ions, the syringe pump was applied to control the releasing rate of silver nitrate in order to limit the free silver cations in the present solution. However, the process of this method was complicated and easy to be affected by human-made factors, giving rise to the irregular products in the final stage. With the help of chloride ions, the simple set up and the uncomplicated process can ensure a stably gradual release of silver cation during the synthesis reaction.

2.2.2.2 The influence of bromide ions

Similar to chloride ions, bromide ions have been used as a growth agent in the synthesis reaction of AgNWs as well. The influence of bromide ions has been studied for many years. For example, at the early stage, Gedanken et al. [6] used AgBr crystal as a precursor attached with the photographic developer solution to synthesize AgNWs. As a result, the

yield was relatively low compared to the general method, and many nanoparticles were formed. However, the results showed that AgNWs were very thin with a diameter of about 20 – 30 nm. In addition, Choi et al. [36] used tetrabutylammonium bromide (TBAB) in the synthesis reaction of AgNWs. They found that altering the concentration of bromide ions can change silver nanoparticles into nanowires, and the diameter of these wires was around 40 nm. This shows that the presence of Br^- can have a significant impact on the width of silver nanowires, which could lead to very narrow wires by tuning the amount of bromide ions.

According to Wiley et al., they were able to produce many AgNWs through polyol methods; nevertheless, the width of these AgNWs was too large, making it hard to make transparent conductive films. Afterward, they found that the ultrathin AgNWs were obtained when they employed NaBr in the reaction. By tuning the concentration of NaBr, different morphologies of AgNWs were produced. The SEM graphics are shown in **Figure 7**. They successfully reduced the AgNWs diameter from ~72 nm to ~36 nm by adding the NaBr with a concentration of 1.1mM. However, the more additional of NaBr would lead to silver nanoparticles as the primary products and even no nanowires. It is vital that the concentration of bromide ions need to be controlled. The studies indicated that the dpletion in diameter might be originated by the increasing nucleation reactions, controlling the concentration of silver at the early stage of the reaction. However, the reason that the addition of bromide ions can have such a significant influence on the diameter of nanowires is still unclear.

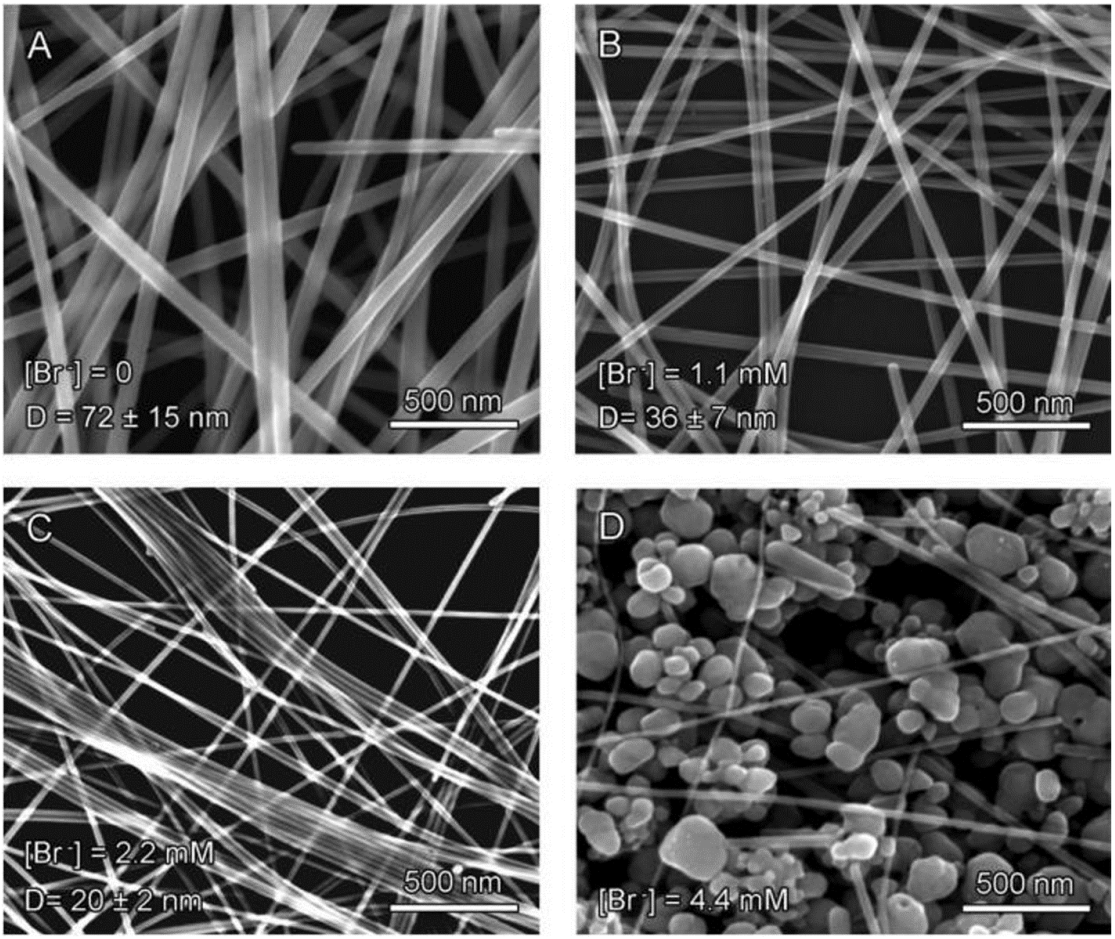

Figure 7 The SEM images of AgNWs with different concentration of NaBr. (A) 0 (B) 1.1 (C) 2.2 and (D) 4.4 mM [19]

2.3 Fabrication methods of AgNW networks

2.3.1 Printing techniques

As mentioned above, there is a trend of making flexible and stretchable conductors in recent years. Since the trend shows up, numerous studies focused on flexible conductor applications have been carried out, such as wearable devices, displays, or touch screens. Most of these foldable, stretchable conductive devices are made from depositing conductive materials onto or into substrates with great flexibility. There are various methods of depositing these materials today, including drop-casting[37], spray coating,

spin coating, and Meyer rod coating[38]. However, there are some limitations among these methods, for example, the slow rate of depositing and high cost, and the most severe problem is the restriction of pattering materials. From this, as the development of fabrication technology, printing techniques such as inkjet printing and electrodynamic jet have emerged recently to improve the drawbacks which are mentioned above. Moreover, these printing techniques could provide great performance in designing and pattering, and the products made from the printing methods could maintain high electrical properties.

2.3.2 Inkjet Printing

It is said that the crucial performance of flexible conductive films is to keep appropriate electrical conductivity when bending or under large deformation. Inkjet printing techniques have been used for making AgNW networks in some studies, and they successfully deposited AgNWs onto substrates and made the conductive films with ductility and flexibility[39-41]. However, this method has some issues, including nozzle clogging. Additionally, it is difficult to print the AgNWs with a relatively high aspect ratio or the AgNWs inks with high concentration. According to Huang, Q et al.[42], because it is hard to deposit high aspect ratio AgNWs through inkjet printing, they used the sonication process first to reduce the length of AgNWs and made them into the inks. After that, they used the ink to deposit the AgNWs onto photo papers and PET substrates **(Figure 8),** and they also successfully fabricated the conductive film based on PDMS/AgNWs in the end **(Figure 9)**. Therefore, due to the high flexibility of PDMS, the PDMS with conductive material AgNWs becomes a stretchable conductive film. However, they found that the sheet resistance will increase after repeated stretching cycles **(Figure 10).** Although this foldable conductor still has challenges that need to be improved and addressed, it shows a great potential to make various flexible conductors

based on inkjet printing techniques once these challenges have eliminated.

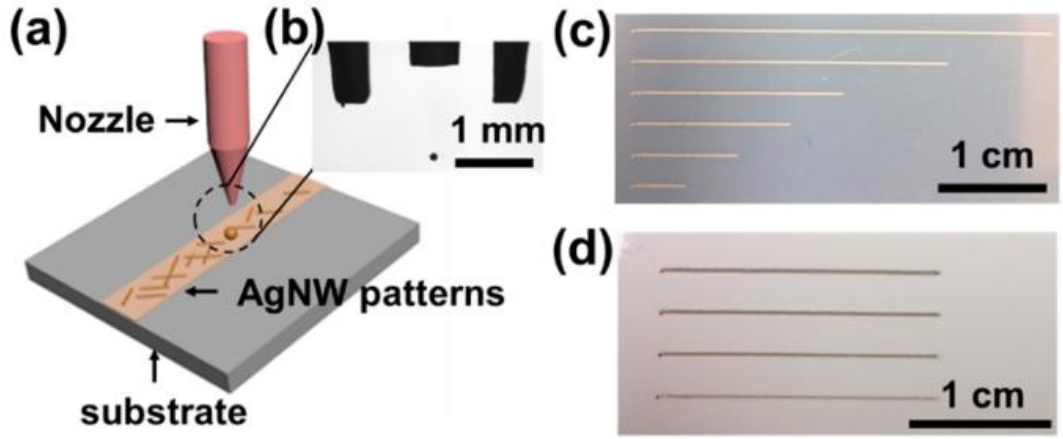

Figure 8 (a) the explanation about inkjet printing (b) image of the droplet during printing (c) the printed line pattern on PET substrate (d) Photo paper [42]

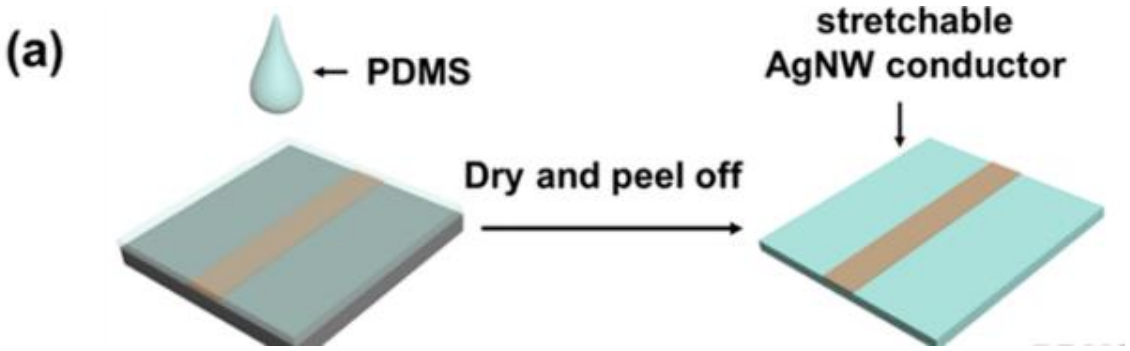

Figure 9 (a) the illustration of making stretchable conductive film [42]

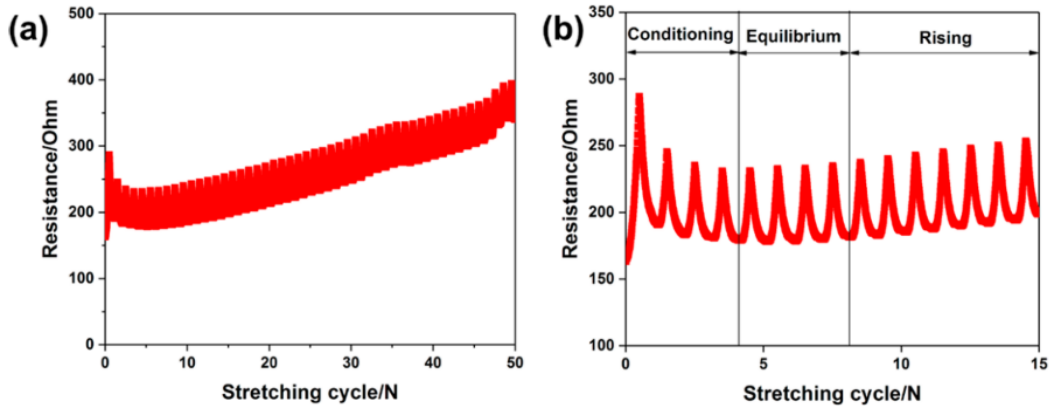

Figure 10 (a) The resistance of AgNWs films versus stretching cycle (b) with three stages [42]

2.3.3 Electro Hydrodynamic Jet

Recently, ever since various flexible conductive films could be directly made from printing devices, many printing technology studies show up rapidly. These printing methods are widely used because they can effectively yield large-area productions with relatively low cost[15]. There are two main printing processes to produce the conductive electrodes: electrohydrodynamic jet (EHD) and inkjet printing[43]. However, compared to EHD, inkjet printing has limitations such as low resolution, nozzle clogging, and difficulty of maintaining the structure's integrity. From this, some printing-related studies have been carried out in recent years. Z.Cui et al.[44] demonstrated three main issues of producing electronic devices through inkjet printing: degradation, low resolution, and ununiform AgNW film structure. To eliminate these problems, they used EHD devices to print AgNWs samples on PDMS substrate with the Peano curve pattern **(Figure 11)**. They also printed AgNW networks on the foldable substrate and tested the flexibility using stretch and bending tests. In **Figure 12**, we can this film shows excellent performance of flexibility. Also, there is one EHD printing study published by Lee et al.[45] found that the characteristics of TCFs can be enhanced by using EHD to print the Ag grids on the ITO substrate. Although the EHD printing method has various advantages such as high

resolution and good structural integrity, some factors may affect the performance of productions. These factors including the applied pressure, working distance to the substrate, speed of printing, nozzle size and so forth.

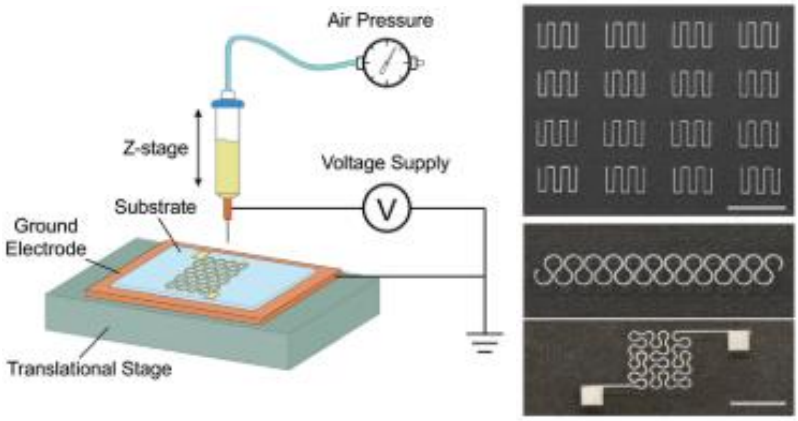

Figure 11 The images of EHD device and different printing pattern including Peano curve [44]

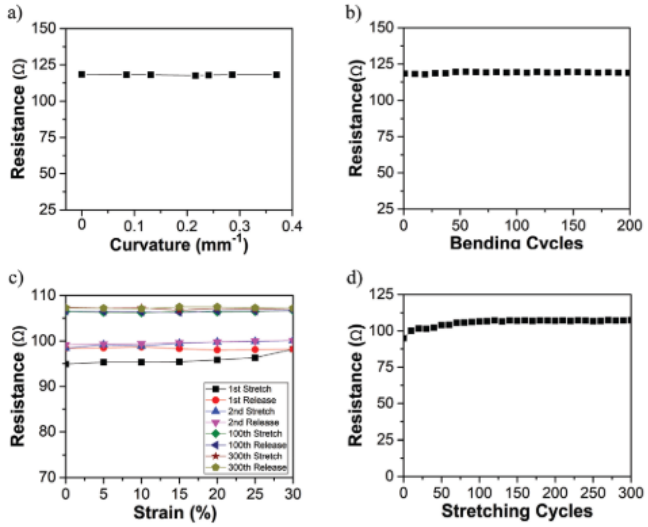

Figure 12 Pattern of AgNW under bending and stretching tests. Resistance versus (a) Curvature (b) Bending cycles (c) Strain(%) and (d) Stretching cycles [44]

2.4 Properties

2.4.1 Electrical properties

The electrical properties take an essential role in the TCFs based AgNWs networks. The different characteristics of AgNWs themselves and morphology lead to various electrical properties of AgNWs networks[46]. Generally, the increase of AgNWs aspect ratio leads to the decrease of the resistance of AgNWs networks[19], which means that it remains a need for generating AgNWs that are both very thin and very long to have an excellent performance of high conductivity. Besides, Bid et al. [47] demonstrated that the reduction of nanowires in diameter will decrease the free path for its electrons and increase resistance. In terms of this, surface scattering becomes the prominent role of electrons movement. The control of AgNWs' length and diameter shows a crucial part for the adjustment of conductivity in TCFs based on silver nanowires.

Many different types of AgNWs based TCFs are made through various fabrications, including drop-casting[48], Mayer-rod-coating[49], spray coating[50], or printing techniques[44]. Previous studies have indicated that as the nanowires' density increases, the resistance of TCFs will reduce and achieve great electrical performance; nevertheless, this also leads to a reduction of the light transmittance[51]. It is crucial to make a counterpoise between electrical and optical performance for generating TCFs. Due to this challenge, many studies have been conducted to modify the balanced properties with various methods to reach great performance. AgNWs is a good conductive material with great electrical properties, but if the junctions of AgNW networks are not attached well, it would increase the resistance and affect the performance of TCFs. According to Hauger,

T. C. et al. [52], the crossover points among AgNWs networks can be affected by temperature, pressure, and rolling speed. If the attachment of intersection points is strongly connected, the networks can have a lower resistance. They announced a method using a roller to roll onto the silver nanowires **(Figure 13a)** TCFs on the hot plates **(Figure 13b)** and optimized the electrical performance by controlling the pressure, temperature, and speed of rolling **(See Table 2)**. The examples of silver nanowires networks with rolling and without rolling are provided in **Figure 14**.

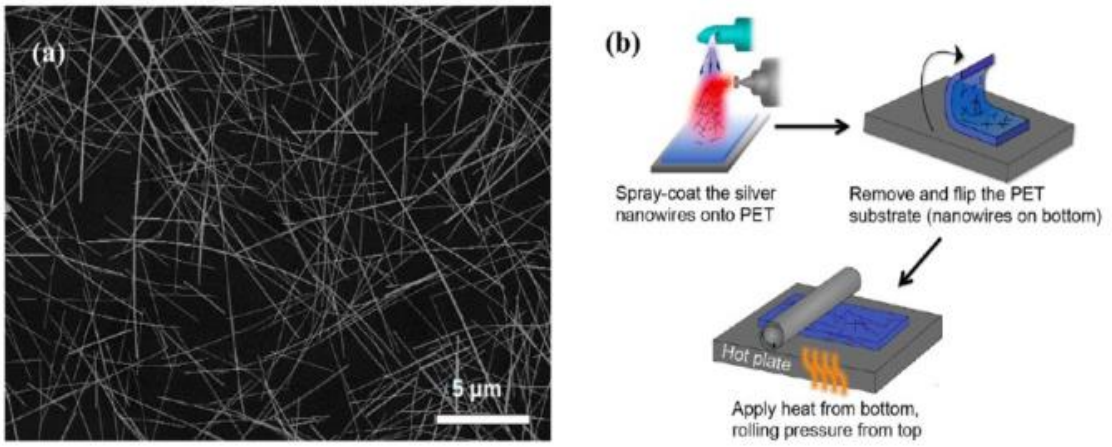

Figure 13 The outline process of using roller method. (a) SEM image of AgNWs in this method. (b) AgNWs are coated on a PET substrate, peel off the PET substrate with AgNW networks and put on a hot plate and use the roller to give it pressure and speed at different temperature [52]

Table 2 Influence of Rolling Speed, Pressure and Hot plate's temperature on the resistance of AgNW networks on PET substrate.[52]

substrate	Speed (cm/s)	Pressure (psi)	Resistance (Ω/sq)
Annealed at 165 ℃			370 ± 130
Rolled at 165 ℃	10 ± 2	50 ± 25	36 ± 3
Rolled at 165 ℃	1 ± 2	50 ± 25	35 ± 15
Rolled at 165 ℃	10 ± 2	250 ± 50	173 ± 83
Rolled at 165 ℃	1 ± 2	250 ± 50	Open circuit

In a short summary of this section, the electrical properties of TCFs based on silver nanowires largely depend on the length, diameter, and aspect ratio of AgNWs. However, after coating AgNWs on the substrate, the connection of AgNW meshes might be weak, which can result in high resistance of these conductive films. Therefore, many studies, such as rolling silver nanowires electrodes[52], have been introduced to address this issue. These modifications can build more robust intersection points of networks and lead to a low sheet resistance for practical applications.

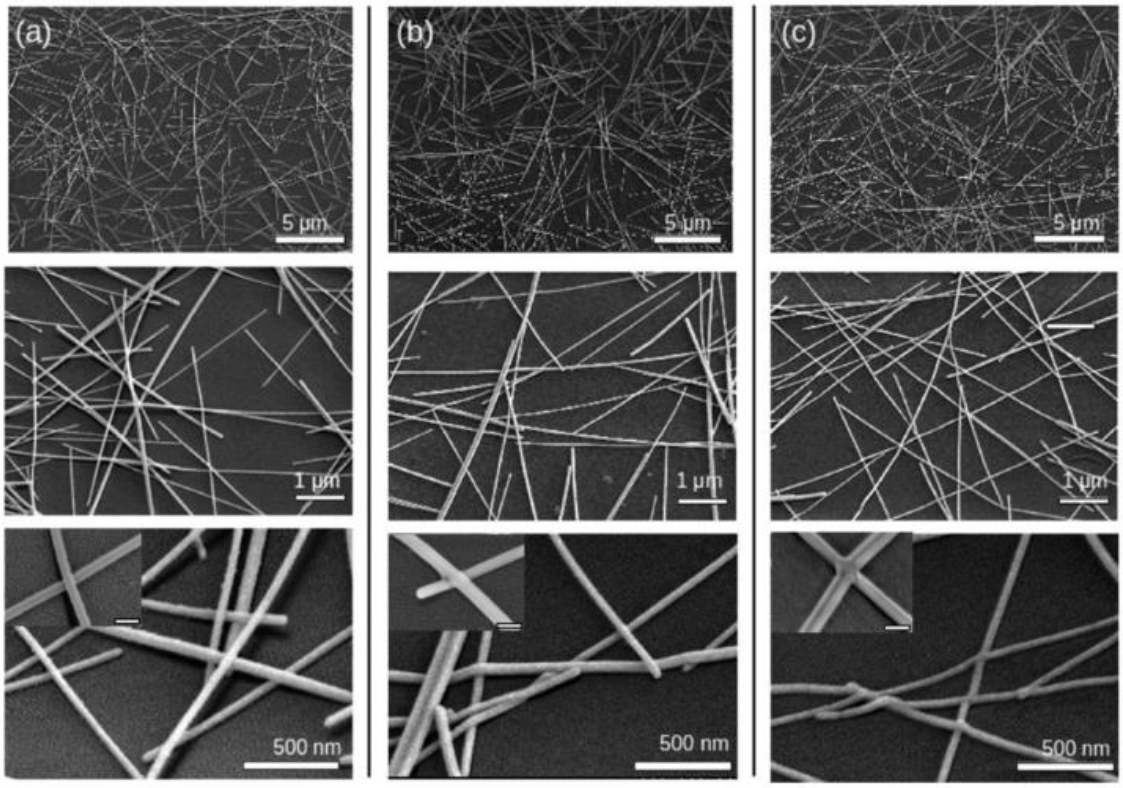

Figure 14 SEM images of PET substrate with AgNWs (a) AgNW networks without rolling (b) AgNW networks with rolling at temperature 60 °C. (c) AgNW networks with rolling at temperature 165 °C [52]

2.4.2 Thermal Properties

Many studies have researched about conductive polymer in recent years. These studies

focus on thermal conductive materials, including silicon dioxide, aluminum nitride (AIN), graphite, or carbon nanotubes embedded into polymer composites due to their easy modification of conductivity and excellent performance corrosion protection. However, the amount of these materials needs to be relatively high to achieve a good thermal conductivity performance. Moreover, the increase of conductive fillers in polymer results in a decrease in their transmittance.

Due to the limitation of the amount of fillers, the thermal conductivity property of these composites might be hard to be improved or enhanced. Therefore, many researchers have started to change their attention to AgNWs films with both transparency and conductivity features [51]. Park, J. W. et al. [1] compared the transmittance, heat dissipation and emissivity of the AgNW networks coated to the glass substrate with other polymer composites filled with thermally conductive materials **(Table 3)**. In general, the emissivity of metals such as Cu, Al or Ag would be relatively low; the emissivity of AgNW films largely depends on its sheet resistance, and as the sheet resistance increases, the emissivity decreases. This table demonstrated from Park, J. W. et al. [1] shows that the AgNW films could achieve great heat dissipation and good emissivity while

Table 3 The measurement of transmittance, heat dissipation and emissivity in different samples [1]

Samples	Transmittance (%, at 520 nm)	Heat dissipation (°C)
PMMA:AlN 5 wt%	49.8	0
PMMA:SiC 1 wt%	46.2	50.1
AgNWs 4 Ω/□	65.5	51
AgNWs 9 Ω/□	77.1	53.7
AgNWs 45 Ω/□	86.6	40
Cu strip lines	–	69.3
Cu sheet	–	102.9

Samples	Emissivity (ε)
Glass only	0.85
PMMA	0.90
PMMA:AlN 25 wt%	0.87
PMMA:SiC 8 wt%	0.88
AgNWs 45 Ω/□	0.73
AgNWs 9 Ω/□	0.52
AgNWs 4 Ω/□	0.32

maintaining relatively high transmittance between (65.5-86.6%). The sheet resistance of

AgNW film largely depends on its density, and as the density in AgNWs is increased, resistance of AgNWs will decrease. In addition, it is believed that during the heating, they would have some changes which may cause the AgNWs to become unstable. These instabilities may considerably change the conductivity of AgNW films. To avoid these issues and enhance the electrical property of AgNW network, the controlled conditions are needed. Although AgNW films have these limitations, nevertheless, the AgNW film with low sheet resistance seems to have the best thermal and optical properties compared with other composite films.

Because of the excellent optical and electrical performance of AgNW films, these films could have a great potential of being used in many thermal conductive applications such as defrosting, defogging windows, or displays in the future.

2.5 Applications

2.5.1 Transparent Heaters

One of the first applications of transparent heaters was the defrosting windows using on the airplane. Today, the use of transparent heaters has spread in various industrials. The traditional film heaters are mostly made of alloy or Indium Tin Oxide; however, there is some weakness of using these two materials. For example, the alloy has a low heating efficiency, and ITO's texture is brittle and easy to break when bending it. As mentioned above, most of these traditional materials are hard to maintain their performance under physical force. Therefore, AgNWs have recently shown up as a promising candidate due to their outstanding conductivity, high transparency, and suitable mechanical properties.

These characteristics can greatly apply to transparent conductive films and make them into flexible transparent heaters. The main principle of operating heaters is based on Joule's heating law, which explains how the electrical current flows will transfer the heat energy. Once the electrical current flows through conductors, the electrical power will be converted to heat energy.

Nowadays, the trend of today's technology is to make flexible and wearable devices, which means that these applications are still making changes. Thanks to the AgNWs, various reports have demonstrated AgNW heaters with excellent performance using plastic or glass substrate. Besides, the good connection of AgNW networks enables the delivery of considerable energy at relatively low voltage, which means that they exhibit more potential for practical applications.

2.5.2 Touch Screens

As the development of electronics, many portable devices such as tablets, smartphones, and laptops have changed humans' lives significantly. The touch screen on these devices also plays a vital role in making them easy to operate and makes our life more convenience. The large majority of touch screens today are made of ITO and other transparent conductive materials. However, most of these materials are easy to break whether they suffer external physical forces. Thus, extensive studies addressing these drawbacks have been carried out in recent years.

AgNWs networks is useful for touch displays due to their well mechanical properties, high transparency, and well conductivity. Although the transparency and mechanical

performance of the AgNW network can pass over the old materials, yet the sheet resistance is still relatively high to other optoelectronic devices, which means their conductivity will be affected. Hence, the main issue of making touch screens based on AgNW networks today is to maintain great performance under different factors such as temperature and external force. Therefore, studies of AgNW should pay attention to the ways of making the connection of AgNW network more tightly to enhance their mechanical and electrical abilities.

2.5.3 Electrochemical reduction of CO_2

It is known that global air pollution has been severe recently. The increasing consumption of fossil fuels results in producing a large amount of CO_2 which is one of the leading greenhouse gases. To fight the greenhouse effect, many studies that focus on reducing the CO_2 emission have been shown up these years. It is believed that CO_2 conversion system with low energy consumption could lead to a significant impact on alleviating the greenhouse effect. From this, electrochemical CO_2 reduction shows the potential for energy-efficient CO_2 conversion due to the availability of the usage of green energy such as solar power or hydropower, which has been more mature in recent years. However, due to the low reactivity of CO_2 and experiences competitive HER, the catalyst surfaces on electrochemical CO_2 reduction reaction needs to have high overpotential. Thus, finding the materials with high activity and ability to covert CO_2 into high-value fuels, such as CO syngas, is an important task. There are some metals, including Au and Ag have been used to covert CO_2 into high-value fuels. Nevertheless, due to these metals' insufficient effort and high costs, it is hard to apply them to large-scale applications. Thus, in order to reduce the high costs and the low efficiencies, the catalysts metals with high activity for the CO_2 reduction are highly desirable. It is believed that the different

morphology of noble metals could have a big impact on the activity of the reduction of CO_2. Changing metals into nanostructure or particle sizes has also shown a significant improvement in catalytic activity. The optimal nanoparticle sizes of Au and Ag [53] have achieved the best Faraday efficiency and current density for the reduction of CO_2. Also, the metal nanowires have shown good performance on the electrochemical CO_2 reduction reaction (CO_2RR) due to the size effects. According to Liu et al., silver nanowires with diameters around 25 nm and 100 nm were employed in the CO_2RR. They found that the one with a smaller diameter could greatly improve the rate for CO_2RR. From DFT calculations, it showed that the catalytic activity of the silver nanowires would be affected by their aspect ratio; the higher aspect ratio leads to a better catalytic activity. **Figure 15** shows the results of FEs of CO(%) and EEs(%) between D-25, D-100, and silver nanoparticles. These figures indicated that silver nanowires with smaller diameters could result in higher CO selectively and catalytic activity.

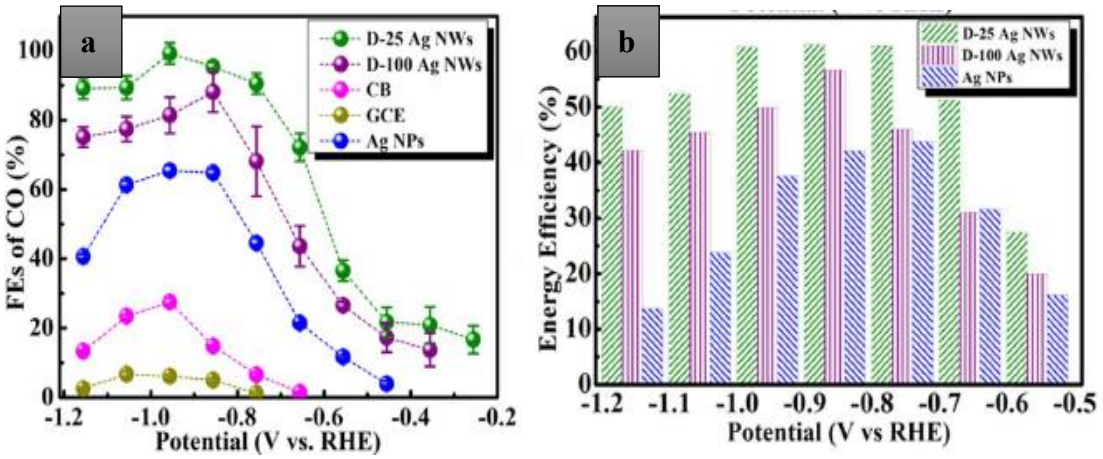

Figure 15 (a) The FEs of CO(%) at among different catalysts at various potentials (b) Energy Efficiency(%) among different morphology of silver at various potentials [54]

2.6 Research gap

AgNWs has been deeply studied over the past many years, a large numbers of synthesis methods, theories and experiments of this material have been demonstrated. Although lots of studies have been reported, there are still some research gaps and issue need to be figured out in the future. For example, more efforts should be focused on other properties of AgNWs, such as adhesion, stability, or surface roughness. In order to apply AgNWs into industry sector, these properties need to be well researched. Besides, it is known that AgNWs are very vulnerable to heat, moisture, and oxygen. The stability and the mechanism during the synthesis reaction and the degradation after becoming the AgNWs TCFs are still not clear. Therefore, more theories and the experiments of these prospects should be focused more in the near future to improve the stability of AgNWs. Moreover, printing techniques will be the technical trend to the future optoelectronic devices. From the previous studies, AgNWs are known to be the printing functional material. However, many issues of applying AgNWs to printing technique, are still hard to solve. To make a large scale of AgNWs based-devices fabrication and improve the uniformity of AgNWs networks, new techniques or the solutions of these issues need to be carried out to push the development of AgNWs based-devices into industrial production.

2.7 Conclusion

In conclusion, the use of AgNWs in advanced electronic devices have been enhanced rapidly and it is still growing at a fast pace. There are many researchers have found and demonstrated AgNWs with good performance in electrical and optical properties. Moreover, due to the great mechanical, thermal and chemical properties of AgNWs, they have the potential of making more advanced and technological electronic devices with

high flexibility and portability. From this, AgNWs are believed to be the most suitable candidate for the replacement of the traditional transparent conductive material-ITO in the future. In this review, I have initially reported the most widely used synthesis method of AgNWs and also presented the purification procedure for the properties' improvement of AgNWs. Next, the two printing methods (Inkjet printing and Electro Hydrodynamic Jet) for the fabrication of AgNW networks were discussed and compared. Finally, electrical and thermal properties of AgNWs have been introduced and discussed. AgNWs are suitable for use in various electronic devices due to these great properties, which can lead to a significant change in our life.

On the other hand, AgNWs indeed possess the great ability to make flexible electronic devices; however, the manufacture of traditional ITO is too mature to make the change for it. The large majority of electronic devices are now made of ITO, and if the replacement of ITO is needed in the future, it is necessary to realize the large-scale fabrication of high-quality AgNWs. Lastly, it is expected that AgNWs could lead to a big change in society. Once the large-scale industrialization of AgNWs becomes mature, it will bring considerable success and profits to the world.

3. Synthesis of Silver Nanowires via Solvothermal Method

3.1 Introduction

Over the past few decades, advanced devices start emerging to the world, such as smartphones, tablet computers, transparent body sensors, and transparent heaters. These devices keep showing up and gradually changing human beings' original lifestyle, which causes the high demand for transparent conductive films (TCFs). Nowadays, the primary material for making TCFs is indium tin oxide (ITO). ITO films possess outstanding electrical conductivity under a high transmittance and can easily apply to various electronic devices. Although ITO offers excellent performance on TCFs, its drawbacks of expensive cost, rigid and brittle are not suitable for making the next-generation intelligent devices that need flexible, stretchable, and low costs TCFs. From this, the materials with benefits of cheap and high performance in electrical conductivity and transmittance, such as silver nanowires (AgNWs), copper nanowires (CuNWs), carbon nanotubes (CNT), graphene[55], and conductive polymers[56], have shown up rapidly in recent years to act as the replacement of ITO. Among these candidates, AgNWs have performed excellent outcomes with inexpensive processing. These abilities enable AgNWs to become the most promising materials for making next-generation TCFs.

Many studies of the Ag NWs synthesis have been carried out over the past few years, and the polyol process is the most common method to prepare AgNWs. However, it is known that there are still some issues of producing AgNWs among these studies, such as stirring

and injection speed. These issues, therefore, cause a significant impact on the morphology of AgNWs and the stability of the synthesis reaction, which leads to the considerable uncertainty of synthesizing AgNWs during this method. Therefore, a convenient and straightforward solvothermal process was carried out, and this method can achieve an easy one-step synthesis without any injection steps. Extensive studies about solvothermal synthesis of AgNWs have been reported recently. However, in the review, there are just a few reports that used salt additives to control the growth of AgNWs, and synthesizing AgNWs with diameter <50 nm or length >100 um through this method is still tricky. Several works via this method have been shown in **Table 4**.

Table 4 Comparison of AgNWs through the solvothermal process

METHOD	DIAMETER(NM)	LENGTH(UM)	ASPECT RATIO	REFERENCES
SOLVOTHERMAL METHOD	910	31.2	35	[57]
	200-250	10-25	40	[21]
	50-100	5-10	50-200	[58]
	56-84	8.6-30	100-550	[59]

According to Fang et al.[57], they successfully prepared a wire-like structure through the solvothermal process, and the mean diameter and length of the final AgNWs are 910 nm and 31.2 μm respectively, and the corresponding aspect ratio was only around 35. Banica et al.[21] demonstrated a two-step solvothermal method by controlling solvent composition to synthesize AgNWs with diameter between 200 - 250 nm, length between 10 - 25 μm and aspect ratio range from 50 - 200, which is still far below the requirement. Liu et al.[58] conducted the solvothermal process to synthesize AgNWs with diameter from 50 – 100 nm and length from 5 - 10 μm. The AgNWs with diameter of 56 – 84 nm and length of 8.6 - 30 μm were synthesized by Chen et al.[59] through a solvothermal

method and had a relatively higher aspect ratio of 100 - 500 than the works mentioned above.

It is known that the salt additives, such as KBr, NaCl, NaBr and $FeCl_3$ can prevent the nucleation of silver ions which will control the releasing rates of silver ions and promote the growth of silver nanowires. However, there are few works using salt additives to make and analyze AgNWs through the solvothermal method. Although some of the mechanisms with these salt additives in the reaction are still unclear, the change of AgNWs with these additives can easily be observed, which is beneficial for the analysis and comparison. Herein, we successfully synthesized AgNWs with diameter from 49 – 113 nm, length from 26 - 89 μm, and aspect ratio ranging from 367 - 1023 via the solvothermal method with dual ionic assistants (NaBr and NaCl).

3.2 Method

3.2.1 Materials

Silver nitrate ($AgNO_3$), Sodium Chloride (NaCl), Sodium Bromide (NaBr), Polyvinylpyrrolidone (PVP, Mw=50,000/ 360,000/ 13,000,000), Ethylene glycol (EG, 99.8%), Absolute ethanol (EtOH). All chemicals were used without any purification and purchased from Sigma-Aldrich. Containers were washed with deionized water (DI) and ethanol and dried by nitrogen gun.

3.2.2 Experimental method

3.2.2.1 Preparations of silver nanowires

Silver nanowires were obtained through a dual ionic assisted process with three-step procedure. The process is shown in **Figure 16.**

The First Step:

From previous studies, it is believed that it can lead to better aspect ratio in average when the molar ratio of NaCl/ NaBr tuned to 2/1. Therefore, in my works, two high concentration solutions were firstly prepared, one with 0.025 g NaCl in 5 mL EG and the other with 0.0216 g NaBr in 5 mL EG. Mix different amounts of the two solutions with 9 mL EG in a sample tube.

The Second Step:

Use a stirrer and a hot plate to stir and heat to dissolve 0.695 g of PVP in 15 mL EG to obtain the homogeneous solution. After the total dissolution of PVP, the solution needs to be cooled down to room temperature. 0.112 g silver nitrate is added into the solution and then the solution is stirred for 10 minutes. Later, the mixed solution of NaCl and NaBr is added into the former solution. After magnetically stirring for another 5 minutes, a translucent suspension was observed.

The Third Step:

Transferred the second step-mixed solution into a Teflon vessel and put it into autoclave and heat at 170 °C for 2 hr 10 min at the thermo-mighty stirrer without stirring. After the

reaction finished, the Teflon vessel was taken out and cooled down to room temperature.

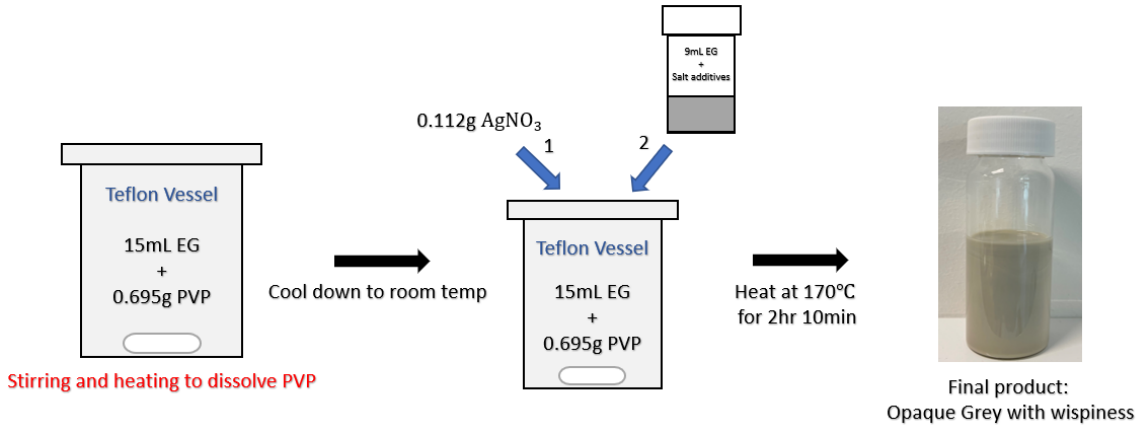

Figure 16 Process of synthesis of AgNWs

After the completion of the reaction, the final product needs to cool down under room temperature. The initial silver nanowires solution was washed through centrifugation at 4000 rpm for about 4 min with ethanol 3 - 5 times to eliminate impurities. **(See Figure 17).** Finally, the purified AgNWs were stored in ethanol for future use.

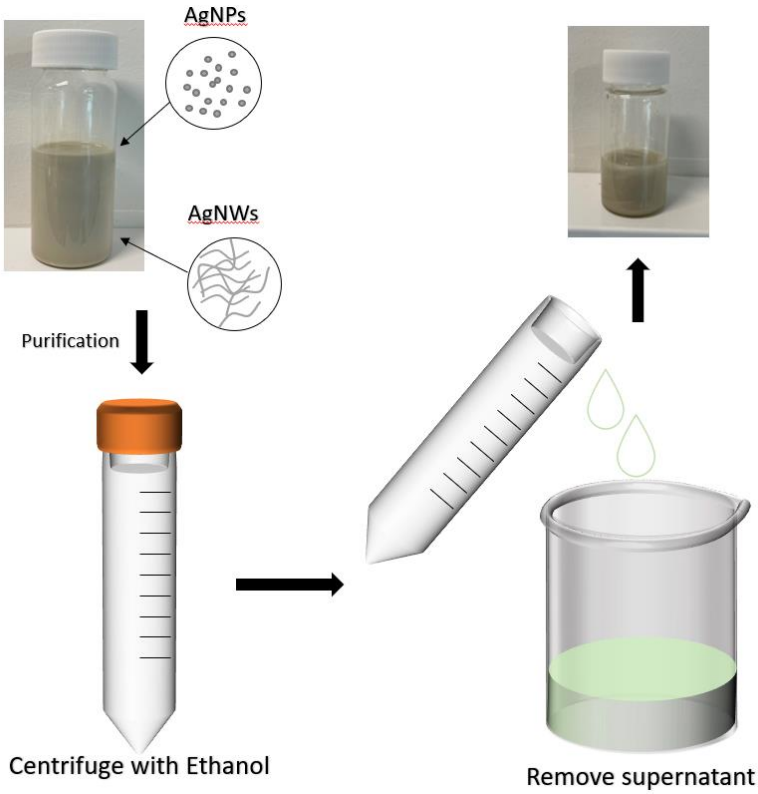

Figure 17 Illustration of washing process of AgNWs

3.3 Result and discussion

Many parameters could affect the morphology of AgNWs significantly. In our works, a large number of experiments were carried out to prepare silver nanowires with a high aspect ratio, as shown in **Table 5.**

Table 5 Parameters we have tested in the synthesis of AgNWs through the solvothermal method

Solvothermal Process	**EG**	**PVP**
PVP dissolving temperature	60 ºC -150 ºC	
Reaction time	1h50min-2hr30min	
PVP Mw	55000,360000,1300000	
M(PVP):M($AgNO_3$)	9.5-7.0	
Direct agent	NaCl / NaBr / NaCl & NaBr	

The experiments under different conditions and their characterization are provided and analyzed below. In this work, we successfully used dual salt additives (NaCl & NaBr) to produce the silver nanowires with a high aspect ratio of 1023 through the solvothermal method **(See Figure 18)**. Besides, the length and the diameter of AgNWs were on average 88.43 μm and 86.5 nm respectively, and the length of AgNWs is relatively higher than other studies.

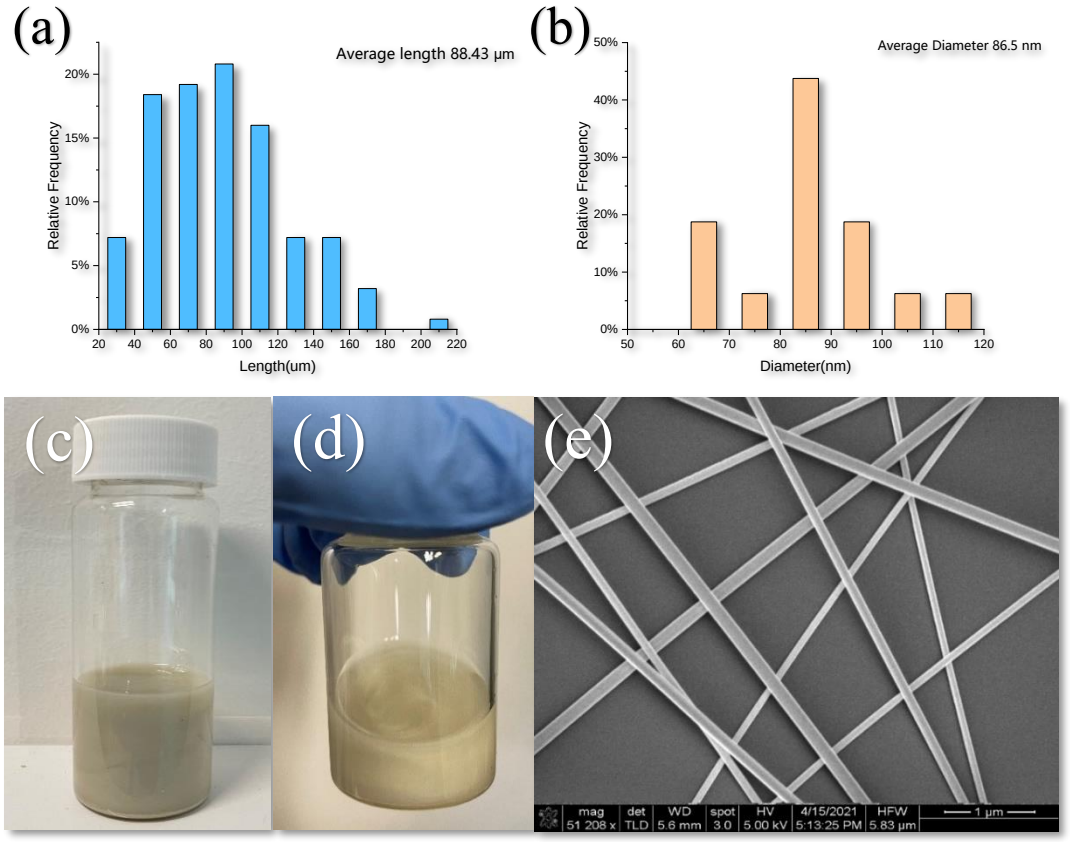

Figure 18 (a) Average length and (b) diameter; S3 AgNWs solution (c) before washing and (d) after washing (g) SEM images of S3 AgNWs

3.3.1 Heating temperature of dissolving PVP at the first stage

From **Figure 16**, the first step of the AgNWs synthesis is to dissolve PVP in EG. According to the previous study, ethylene glycol (EG) was acted as a reduction agent and a solvent to produce AgNWs with uniform morphology and size in the presence of PVP. The molecular weight of the PVP we used in the reaction is 360000. Due to such a high molecular weight, it has a high viscosity, and it is easy to agglomerate when put into water or alcohol, which leads to the slow dissolution of PVP at room temperature. Thus, dissolving PVP with the help of heating and stirring is needed. The boiling point of EG is around 197 ºC, so the temperature should be carefully controlled under 190 ºC. We tried three different temperatures to dissolve PVP at the same stirring rate and found that the diameter of AgNWs increased when the temperature increased, as shown in **Figure 19**. However, when the temperature was controlled at 60 ºC, it took too long time to dissolve PVP. It is hard to make sure whether the PVP is entirely dissolving in the EG solution at this low temperature, and it usually leaves some PVP particles at the final stage. Moreover, although the PVP dissolution process was fast when set the temperature at 150 ºC, the synthesized AgNWs exhibited a larger diameter (91.5 nm) than others which may be hard to achieve the high aspect ratio at the end of synthesis. Besides, EG might be reduced at 150 ºC, which leads to a lack of reduction solvent to generate silver atoms. We also found that the silver nanoparticles increased when setting the dissolving temperature at 150 ºC. Therefore, in the following experiments, we controlled the dissolving temperature at 90 ºC for speeding the dissolution rate and avoiding the thick AgNWs. The comparison also shows that the higer aspect ratio was obtained when conducted the dissolving temperature at 90 ºC.

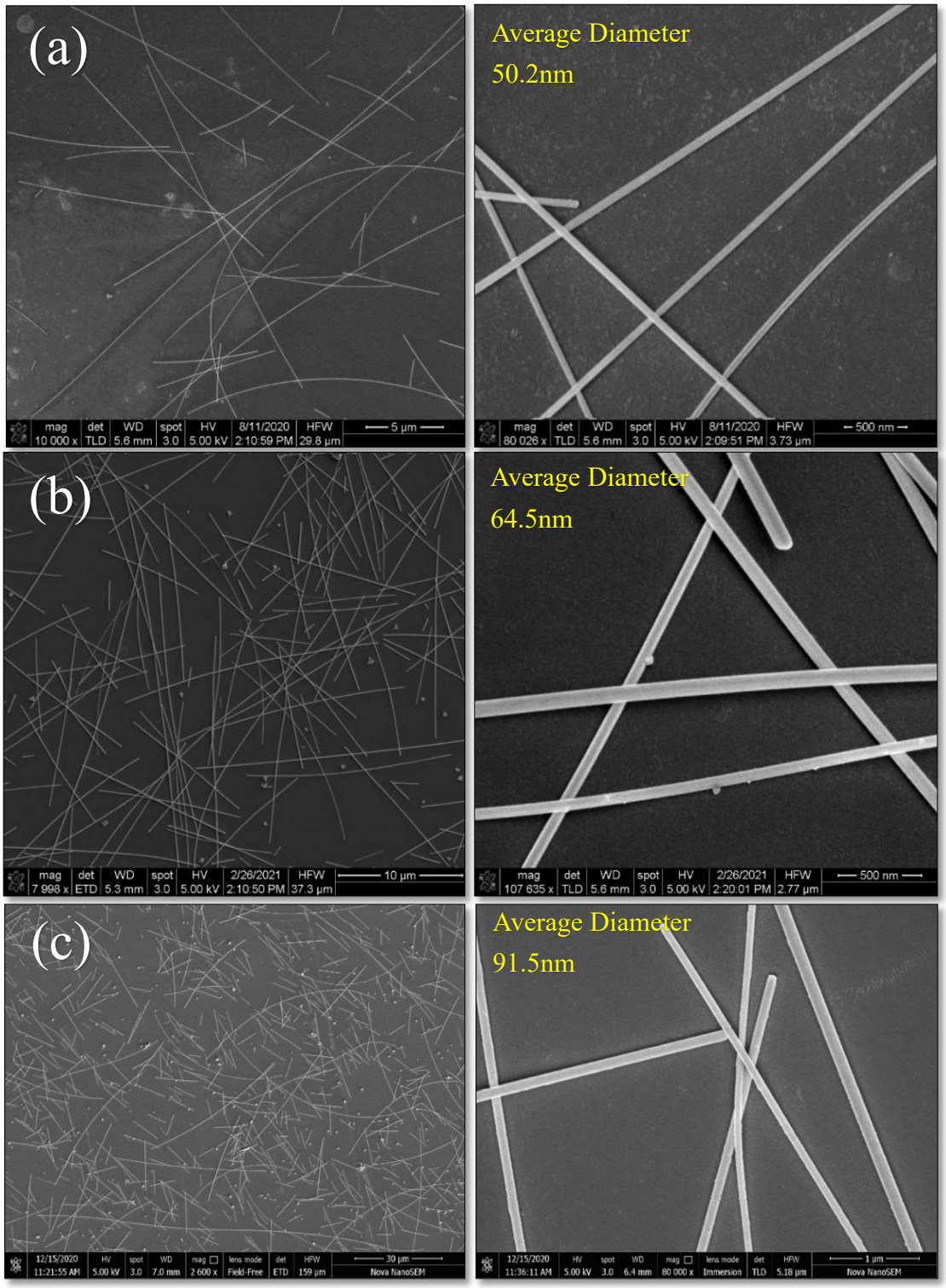

Figure 19 AgNWs SEM images from solvothermal process with different PVP dissolution temperatures (a) 60 ºC (b) 90 ºC (c) 150 ºC

3.3.2 The molar ratio of PVP to $AgNO_3$

Polyvinylpyrrolidone (PVP) was used as a capping agent to synthesize AgNWs. It is currently the most common polymer for assisting the growth of AgNWs. The role of this polymer is to attach to the surfaces of nanoparticles or seeds and direct their growing direction. Many studies indicated that there were various ways to influence the morphology through PVP, including using the different molecular weight of PVP and tuning the molar ratio between PVP and $AgNO_3$.

In our works, we did not take too much focus on tuning the molar ratio of PVP to $AgNO_3$. However, because the amount of PVP we used in our reaction took too long to dissolve, as section 3.3.1 mentioned, we adjusted the molar ratio of PVP/ $AgNO_3$ from 9.45 to 7. We found that the diameter increased from 64.5 to 82 nm, but the length did not have any apparent change, which causes the aspect ratio to be lower than the previous experiment **(Figure 20)**. Thus, we did not take further research on this factor in the following synthesis.

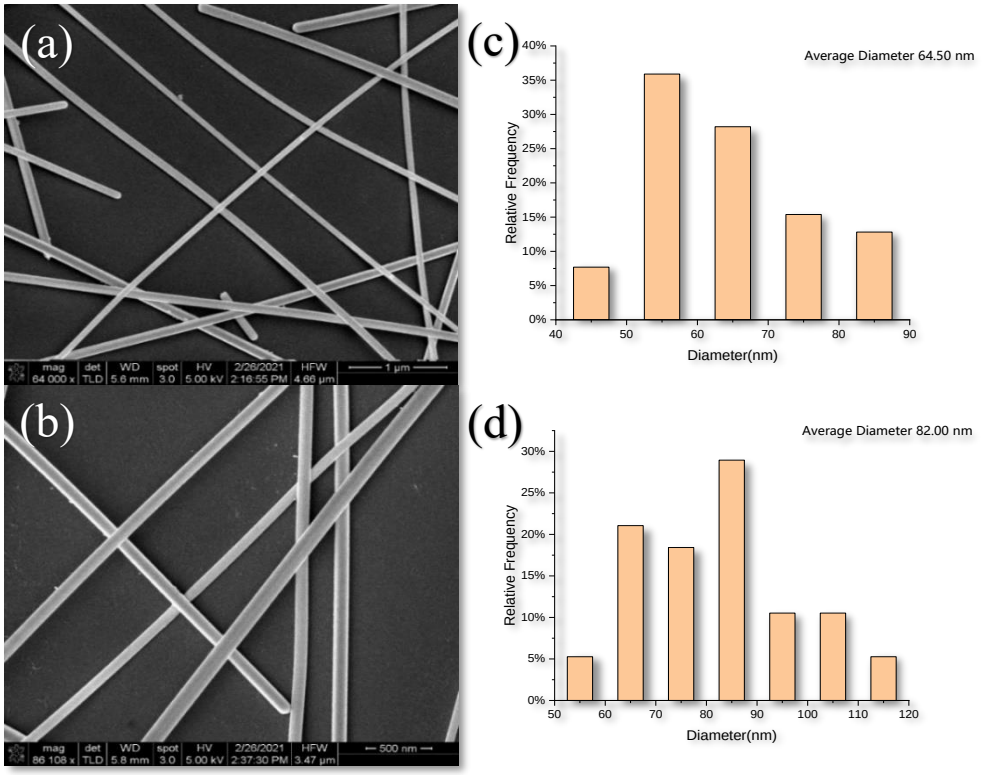

Figure 20 The SEM images of different molar ratio of PVP to $AgNO_3$ (a) 9.45:1 (b)7:1 and their diameter comparison (c,d)

3.3.3 The molecular weight of PVP

In terms of the growth and reduction in the process, EG is generally used as a reducing agent, and PVP plays the role of capping agent during the reaction. The anisotropic growth mechanism of Ag nanowires produced by polyol method is that PVP interacts more strongly with silver atoms on the {1 0 0} facets than {1 1 1} facets, which slows the growth rate on {1 0 0} facets and facilitates the anisotropic growth on {1 1 1} facets[3]. According to the previous studies, the chain length of PVP showed a significant impact on navigating the growth of Ag nanostructures. Zhu et al. have investigated the effect of chain lengths of PVP on the Ag morphology[30]. From their study, with the increasing molecular weight of PVP from 1500 to 800000, the average length of AgNWs increased from 3 to 10 μm, and the yields of AgNWs improved from 40 to 99%. In addition, the

morphology and size of AgNWs became more uniform when reacting with a higher MW of PVP. Therefore, in our works, we tried three different molecular weights of PVP 55000(S8), 360000(S2), and 1300000(S9) to synthesize AgNWs. We found that longer AgNWs were obtained using PVP with a higher molecular, and there was no significant change in their diameters. However, the high molecular weight of PVP causes slow dissolution in EG at room temperature. Thus, we applied the heating process into the synthesis steps mentioned in section 3.3.1 to enhance the dissolving rate. As a result, we kept other parameters the same (0.18 mM/ 0.09 mM NaCl/ NaBr, reaction time 2 hr 10 min and 0.695 g silver nitrate) and successfully synthesized AgNWs with aspect ratio about 2000 by using 1300000 Mw PVP **(Figure 21)**.

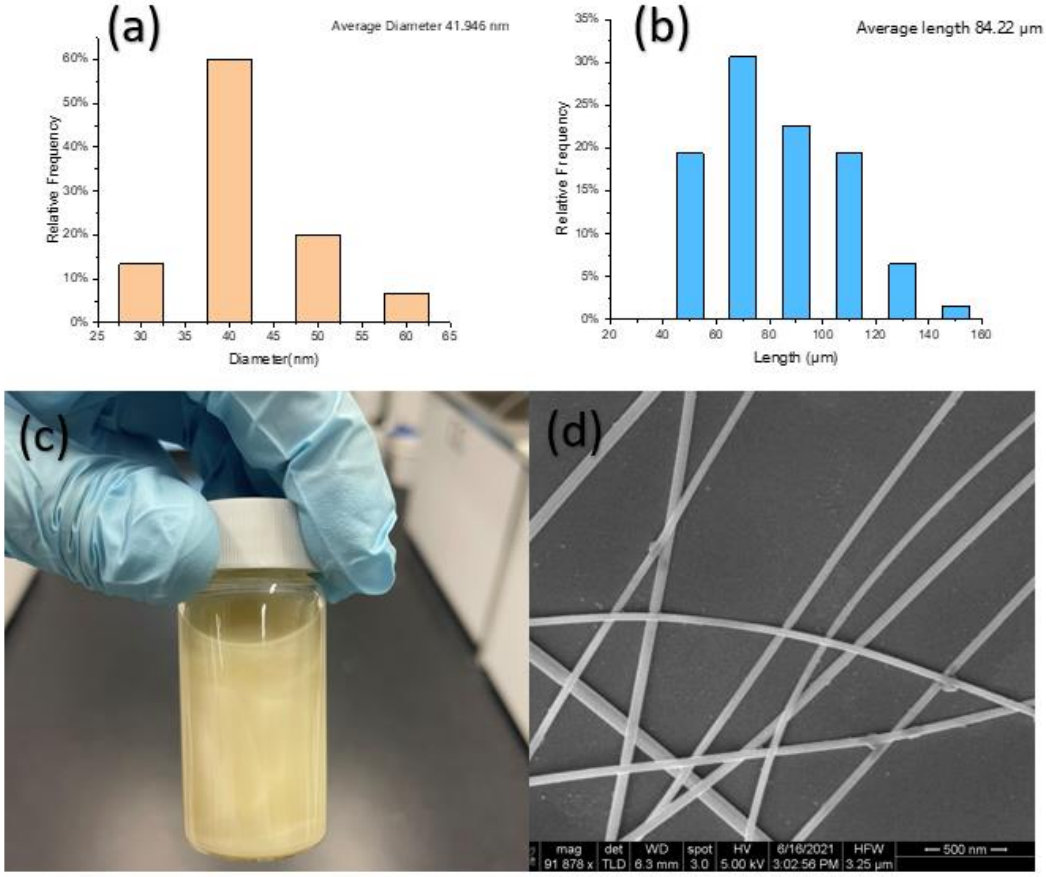

Figure 21 (a) Average diameter and (b) length of S9 AgNWs, (c) as-prepared S9 AgNWs solution, (d) SEM images of S9 AgNWs

3.3.4 Dual Ionic additives in the solvothermal process

The presence of exotic species, such as NaCl [60], KBr, NaBr, $CuCl_2$ [61], and $FeCl_3$ [62], has been widely used to synthesize AgNWs to enhance the aspect ratio and achieve control over their final morphology. It is generally believed that halogen anions, especially chloride and bromide, are essential to prevent Ag seeds' aggregation. The chloride and bromide anions in the reaction tend to form AgCl and AgBr during the process, which acts a similar role as a syringe pump for offering controlled releasing rates of Ag seeds at the initial stages in the synthesis. They significantly decrease the accumulation of plethoric concentration of Ag seeds and lead to a stable release of Ag cations for the stage of nanowires growth. In addition, bromide ions play an important role in reducing the diameter of AgNWs. However, many nanoparticles were observed when increasing the amount of bromide ions [63], which led to low yields of AgNWs. In general, bromide ions cause a dramatic change in the growth of silver nanowires than chloride ions. Thus, few studies conducted the synthesis with only bromide ions. They usually used two or more different additives to control the growth of AgNWs. It needs many experiments and tests to reach the suitable amount that can produce the best aspect ratio of AgNWs when conducting the synthesis with Cl^- and Br^- additives.

Herein, we first synthesized AgNWs (S6) with only one salt additive-NaCl; however, the length and the aspect ratio of S6 were too low shown in **Table 6**. So, we then tried to add two additives-NaCl & NaBr and tuned both concentrations while the other conditions were kept constant. The comparison shows in **Table 6** and **Figure 23**. From the previous studies, many researchers have used a Cl/Br ratio of 2 to generate the ultra-thin AgNWs. According to Rui et al.[60], they claimed that the highest aspect ratio of AgNWs was

obtained by the polyol reduction process when the molar ratio of NaCl/ NaBr was controlled at 2:1. Also, they found that a larger ratio of NaCl/ NaBr will result in the formation of thick AgNWs. In our works, we first synthesized AgNWs with NaCl/ NaBr molar ratio at 2:1, (0.18 mM/0.09 mM) and obtained AgNWs with a diameter of about 64.5 nm and an aspect ratio of 601. We tried to increase the concentration of NaBr & NaCl together and remain the same ratio value, but the final aspect ratio of S4 did not reach our expectations. Afterwards, synthesis experiments with NaCl/ NaBr molar ratio ranging from 1-4 were carried out, as shown in **Table 6 (S1, S2, S3, S5)**.

Table 6 The results comparison with different concentration of NaCl & NaBr

NO.	NaCl(mM)	NaBr(mM)	Length(μm)	Diameter(nm)	Aspect Ratio
S1	0.09mM	0.09mM	74.5	113.5	657
S2	0.18mM	0.09mM	38.43	64.50	601
S3	0.27mM	0.09mM	88.43	86.50	1023
S4	0.27mM	0.135mM	26.4	72.00	367
S5	0.36mM	0.09mM	65.80	103.4	636
S6 (NaCl Only)	0.18mM	X	33.6	66.7	501
S7 (Excessive NaCl)	0.90mM	0.09mM	X	79.2	X

As a result, we found that the diameter increased from an average of 64.5 nm to 86.5 - 103.4 nm with increasing NaCl concentration. The diameter increased from 64.5 nm to 113.5 nm when the molar ratio of NaCl/NaBr is less than 2. Moreover, the length of AgNWs would also increase when the molar ratio of NaCl/ NaBr is above and below 2. Although it could produce AgNWs with a thin diameter when NaCl/ NaBr molar ratio is 2, the length and the aspect ratio were relatively low in our solvothermal synthesis works.

When the NaCl/ NaBr molar ratio reached 3, the AgNWs (S3) with >1000 aspect ratio was obtained. When the concentration of NaCl was tuned to 0.9 mM (S7), which is five times more than S2, the mixture of nanorods and short silver nanowires were formed in the final product **(Figure 22)**. Moreover, the sample S2, in which the molar ratio of NaCl/NaBr is 2, was found to be the most uniform one than others. The nanoparticles and various formation AgNWs seemed to increase when the molar ratio is under and above 2.

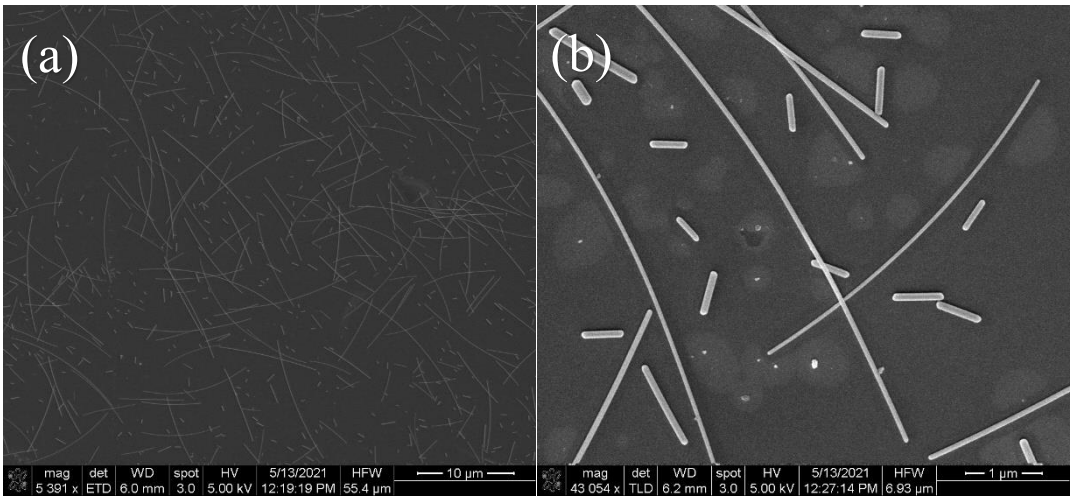

Figure 22 SEM images of the mixture of nanorods and nanowires of S7 (a) 10 µm (b) 1 µm

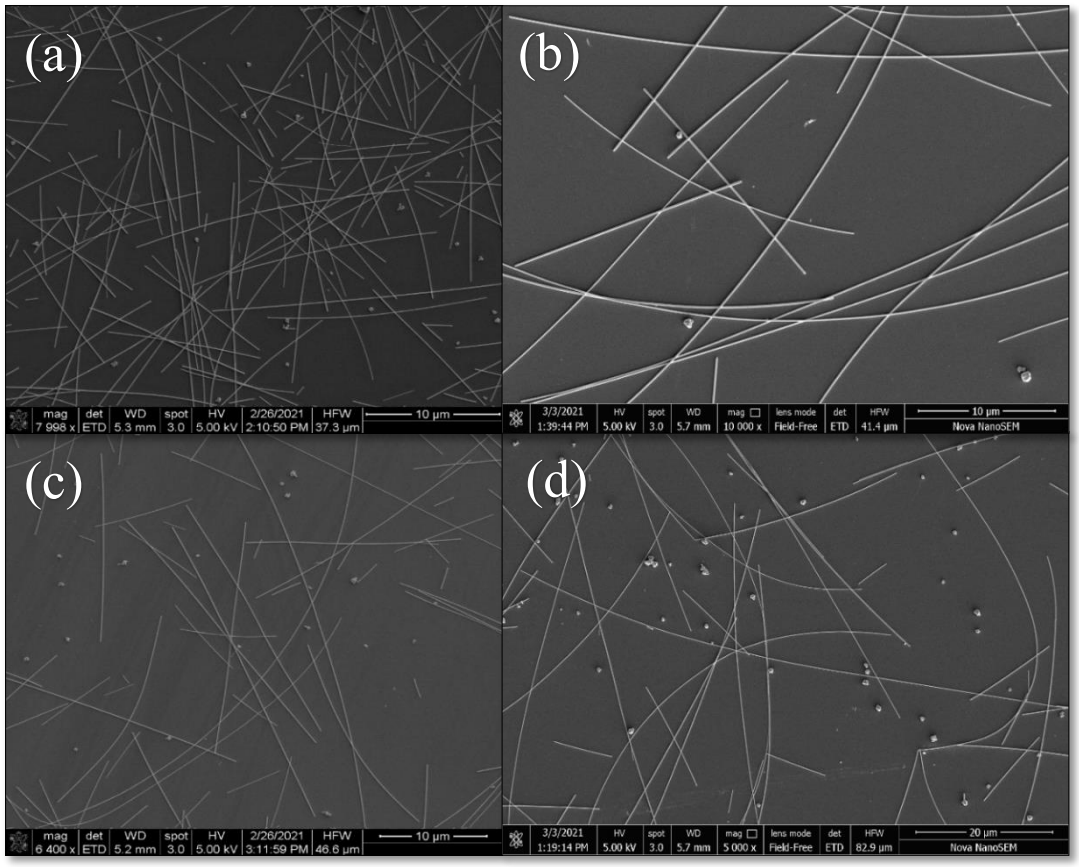

Figure 23 SEM images of AgNWs synthesized by solvothermal with different concentration of NaCl and NaBr. (a) S2 0.18 mM NaCl & 0.09 mM NaBr (b) S3 0.27 mM NaCl & 0.09 mM NaBr (c) S4 0.27 mM NaCl & 0.135 mM NaBr (d) S5 0.36 mM NaCl & 0.09 mM NaBr

3.3.4.1 Analysis of silver nanowires growth mechanism with co-additives

Although it is still unclear why co-additives could obtain AgNWs with an aspect ratio that higher than average, many studies and experiments over the past few years have produced ultrathin-AgNWs and tried to explain their mechanism. In general, it is now believed that the combination of halogen elements and silver, such as AgCl and AgBr, could control the aggregation of Ag cations, which leads to the growth of AgNWs. In our works, the addition of two ionic assistants is to maintain the release rate of silver cations

as well as control the size of Ag seeds. AgCl and AgBr seeds formed at the first stage, preventing Ag cations' aggregation during the heating process. The Ag cations started to be reduced to Ag when the temperature rose to 170 ºC. With the help of a capping agent (PVP), the Ag seeds then grow into nanowires. Moreover, the NaBr plays an essential part in controlling the size of Ag seeds. According to Rui et al.[60], they proposed a mechanism based on FE (ETD) to explain the different Ag seed sizes obtained from AgCl and AgBr **(See Figure 24)**. They demonstrated that the electron traps are mainly located in the interior of AgBr grains, and relatively few Ag^0 are attached on the AgBr surface compared to AgCl, which causes the small-sized multiple twinned particles. However, more silver nanoparticles were obtained when more NaBr additive was added into the reaction because the electron traps are primarily in the interior of AgBr. Therefore, it is important to tune the ratio with NaCl and NaBr to produce silver nanowires with a better aspect ratio (>2000) and less nanoparticles.

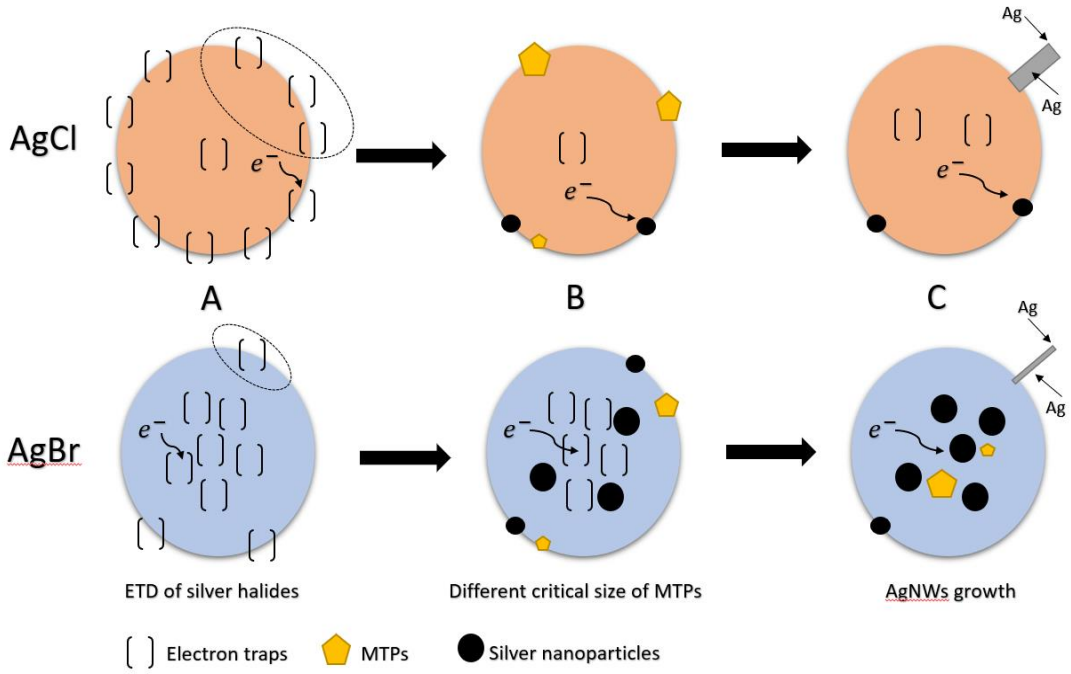

Figure 24 Illustration of the growth of AgNWs with electron trap mechanism for the two types of silver halides

3.4 Summary

We have successfully synthesized AgNWs with a high aspect ratio by mixing the reaction agents (PVP, silver nitrate, EG) and the co-additives (NaCl and NaBr) through the modified-solvothermal process. In our works, we first tuned the dissolving temperature of PVP in order to find the faster way to dissolve PVP at the first stage. Besides, the molar ratio of PVP/$AgNO_3$ and ionic additives have also been investigated in the synthesis to optimize the formation of thinner and longer AgNWs.

In all experiments, the two best aspect ratio we obtained was >2000 (84 μm in length and 41 nm in diameter) and >1000 (88 μm in length and 86 nm in diameter). The diameters of all AgNWs samples were almost under 100 nm, and the thinnest result can be achieved around 40nm. However, some of the length of the thin AgNWs samples were too short of reaching a high aspect ratio. With the change of different factors, the morphology of AgNWs was affected considerably. It is highly possible to make AgNWs with a higher aspect ratio (>2500) and a thinner diameter (<40 nm) through this simple one-step synthesis process by tuning other factors in the future.

4. Synthesis of AgNWs through Maillard Reaction-controlled process

4.1 Introduction

Transparent conductive films (TCFs) have been used in various applications, such as solar cells, body sensors, touch screens, etc. AgNWs is one of the most promising materials for making TCFs in recent years due to their unique properties. Many studies have focused on developing synthesis methods for making AgNWs with better performance over the past few years. The most widely used process for making AgNWs is the polyol process. As mentioned in section 3.1, with the help of PVP (capping agent), EG (reduction agent), silver nitrate (Ag seeds source), and some additives, uniform AgNWs would be obtained via the polyol process.

There are lots of studies focused on tuning the different parameters or adding the other additives to produce AgNWs with better aspect ratio (>2000) and thinner diameter through the polyol method. Besides the polyol method, many other fabrication methods of AgNWs have also been demonstrated, including the hard template method[64], hydrothermal process, and nano porous membranes[65]. However, many of these methods require special reaction equipment and complex process, making these methods inefficient and hard to generate AgNWs with large-scale production. Therefore, developing an efficient, cost-effective, and scalable way for preparing AgNWs with a high aspect ratio is needed.

According to many previous studies, it is believed that the reduction kinetics is a crucial factor in producing ultra-thin AgNWs with a high aspect ratio. It is because controlling the reduction kinetics can affect the size of silver seeds before growing to AgNWs. In the polyol process, the reduction agent is the decomposition products obtained from ethylene glycol (EG) at high temperatures. Due to the reaction at the high temperatures, it is not easy to control the reduction kinetics, and the decomposition process is also hard to control. Besides, when the process is conducted at a high temperature, the growth of silver seeds will be fast, which enlarges the size of the seeds. Therefore, a new approach-Maillard reaction controlled synthesis was demonstrated by Xiao et al.[32]. They successfully produced ultra-thin AgNWs with diameters from 20 – 32 nm. The Maillard reaction is a chemical reaction between reducing sugar and amino acids or compounds. The final products of the reaction include aldehydes and reductones, which have a powerful reducing ability. Xiao and his workers used ammonium bromide and glucose as Maillard reaction agents, in which their final products can react with silver nitrate at low temperatures. From this, the silver seed can keep at a small size because the reducing reaction was reacted at a low temperature, which limited the growth rate of seeds. However, almost no study focused on preparing silver nanowires with the Maillard-reaction method. There are still many factors unclear, and it needs more research and tests to make this process more mature. Herein, we conducted Maillard-reaction controlled process with ammonium chloride and glucose as Maillard-reaction agents to prepare silver nanowires. We tune different parameters and discuss the change in the morphology of AgNWs. Besides, apart from ammonium chloride, we added the second salt additives (sodium bromide) to study the influence with co-additives in this Millard-reaction controlled synthesis reaction.

4.2 Method

4.2.1 Materials

Glucose, ammonium Chloride (NH_4Cl), Silver nitrate ($AgNO_3$), Sodium Chloride (NaCl), Sodium Bromide (NaBr), Polyvinylpyrrolidone (PVP, Mw=360,000), Ethylene glycol (EG, 99.8%), Absolute ethanol (EtOH). All chemicals were used without any purification and purchased from Sigma-Aldrich. Containers were washed with deionized water (DI) and ethanol and dried by nitrogen gun.

4.2.2 Experimental method

We synthesized silver nanowires through Maillard-Reaction Process in two steps **(see Figure 25)**

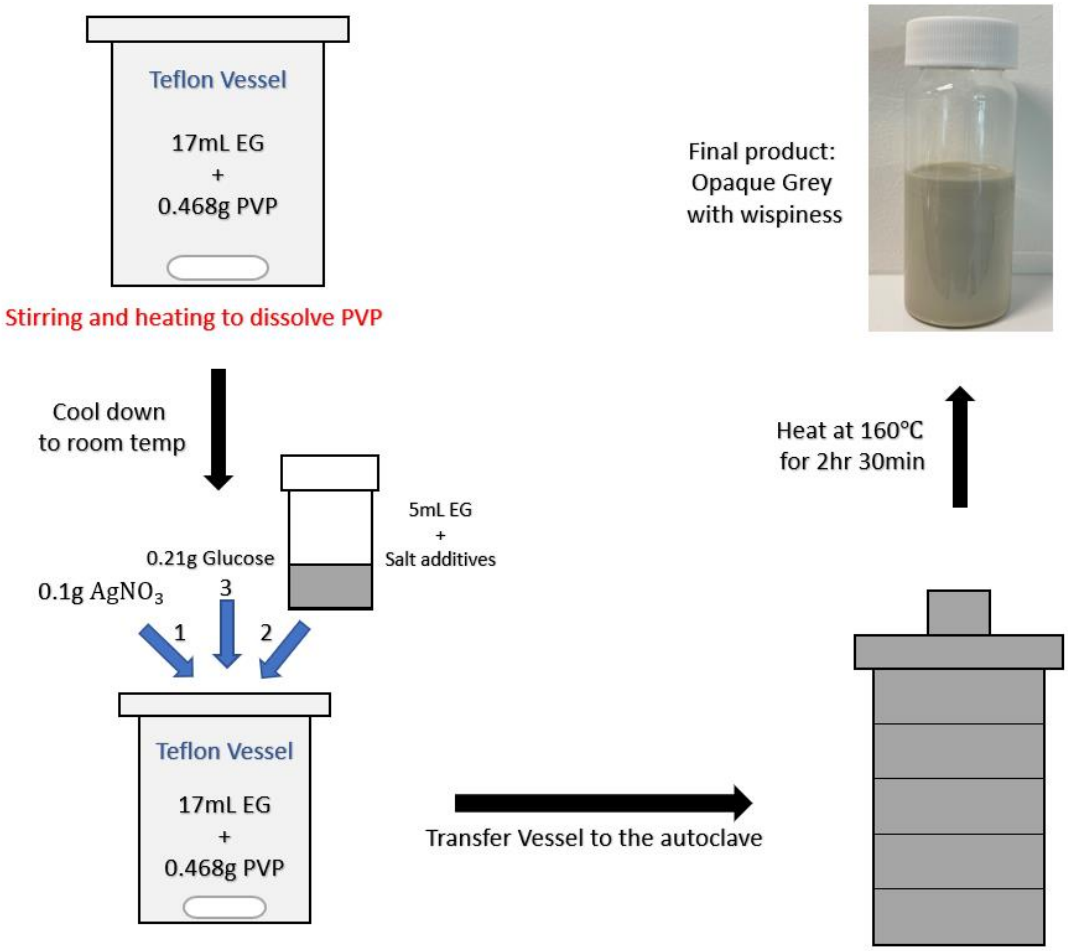

Figure 25 Illustration of the process of Maillard-Reaction controlled synthesis.

The First step:

17 mL of EG and 0.468 g PVP was added in Teflon vessel or beaker, stirred, and heated at 90 ºC for 1 hour to dissolve PVP until the solution clear and no PVP particle inside. Cool it down to room temperature after fully dissolved the PVP. 5 mL EG with 0.00106 g NH_4Cl in the sample tube was firstly prepared.

Second step:

After the solution cooled down to room temperature, the NH_4Cl with EG solution was mixed into the Teflon vessel and kept stirring for 10 minutes. Immediately, 0.1 g $AgNO_3$ and 0.21 g glucose were then added into the vessel and magnetically stirred for another 5 minutes. After finishing stirring and all chemicals were fully dissolved, transfer Teflon vessel to the autoclave and put onto a hot stirring plate and heated at 160 ºC for 2 hr and 30min without stirring.

We also tried to synthesize AgNWs via the Maillard-reaction method without autoclave to see the difference. However, without the help of an autoclave, nanorods and short AgNWs were formed in the final product. See **Figure 26** for the comparison. From this, we could know that pressure in this reaction was essential to obtain the AgNWs in this process.

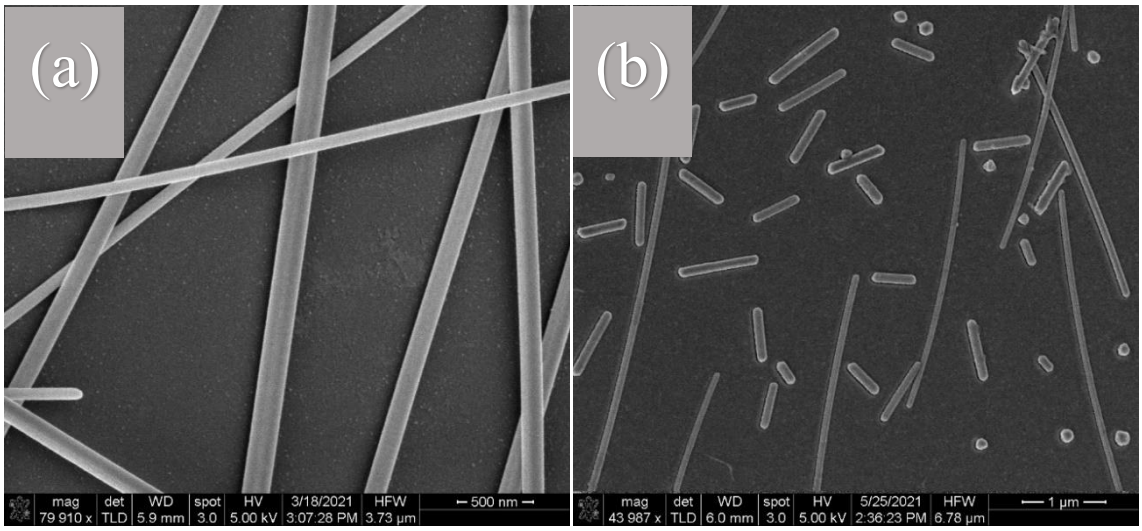

Figure 26 SEM images of AgNWs via Maillard-reaction controlled process with (a) autoclave and (b) without autoclave.

After that, when the reaction was completed, the crude AgNWs solution (opaque grey with wispiness) was obtained. The crude AgNWs solution was then washed with absolute

ethanol through a centrifuge at 4000 rpm for 4minutes for 3 - 4 times, respectively. Finally, the as-washed AgNWs were store in ethanol for future usage.

4.3 Result and discussion

From the previous studies, there was almost no one conducted the AgNWs synthesis with ammonium chloride. As mentioned above, it is hard to control the synthesis through the Maillard-reaction process due to the strong reducing power of MRPs. The purpose of this work is to produce AgNWs through the Maillard-reaction process successfully. Thus, plenty of practical synthesis experiments with different parameters were carried out to see the different results and comparisons. The details of the experiments and the results are shown in the following section for discussion.

4.3.1 The influence of reaction time in Maillard-reaction controlled process

The different morphology of AgNWs can have a significant impact on the optical and electrical performance of AgNWs networks. It is well known that the temperature and the reaction time are the two main factors controlling the dimension of AgNWs. According to Xiao et al.[32], they conducted the AgNWs synthesis at 160 ºC for 2 hours and obtained the best aspect ratio of AgNWs. Therefore, in our works, we first started the experiment with the same temperature and reaction condition. However, there were no silver nanowires observed after 2 hours of reaction. We can observe that the color of the final solution was dark brown/green without any wispiness. Generally, if AgNWs are inside

the solution, the appearance should be opaque grey-green with wispiness like the image shown in **Figure26** and the comparison in **Figure28**. Hence, we could estimate that the primary products in the solution were silver nanoparticles instead of silver nanowires. Moreover, we found that some silver nanoparticles were just ready to grow into nanowires from SEM images **(see Figure 30).** So, it might be that the reaction time was not long enough for silver seeds to grow.

We then tried to increase the reaction from 2 hr to 2 hr 45 min. It was apparent that when the reaction time increased, the amount of the silver nanowires increased until 2hr30min. The comparison results are shown in **Table 7** and **Figure 29**.

Table 7 The AgNWs comparison with different reaction time

NO.	*Reaction time*	*Temperature*	*Mean Diameter (nm)*	*Mean Length (μm)*	*Aspect Ratio*
M1	2 hr	160 ℃	X	X	X
M2	2 hr 15 min	160 ℃	86.50 nm	107 μm	808
M3	2 hr 30 min	160 ℃	106.5 nm	110.05 μm	970
M4	2 hr 45 min	160 ℃	95.5 nm	115.5 μm	825

Besides, the best aspect ratio (970) with length of 106.5 μm and diameter of 110.05 nm was also obtained when the experiment reacted for 2 hr 30 min. Nevertheless, when the reaction time was longer than 2 hr 30 min, the diameter started to grow, and the aspect ratio started to decline. From this, the reaction time for the following experiments was controlled at 2 hr 30 min for further research.

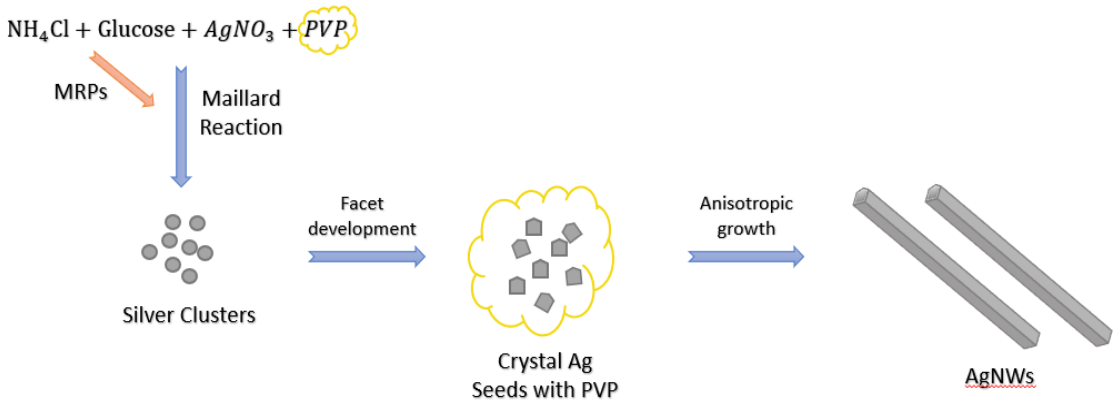

Figure 27 A brief mechanism of Maillard Reaction controlled synthesis of AgNWs

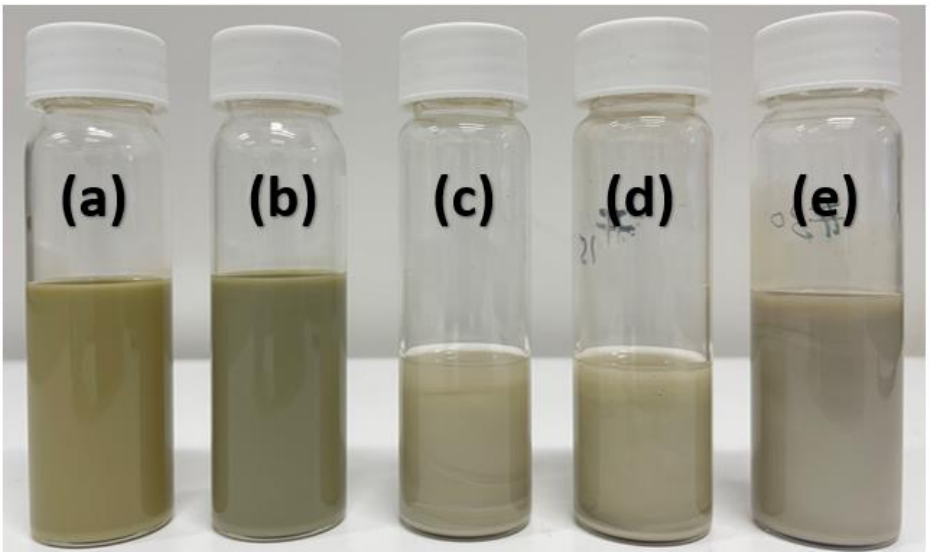

Figure 28 The possible products in the different colors of the final solution after synthesis.

(a) Brown grey (nanoparticles)

(b) Dark green with wispiness (thin AgNWs or nanoparticles)

(c-e) Opaque grey-green with wispiness (AgNWs, if the color is greyer, the diameter of AgNWs might be thicker)

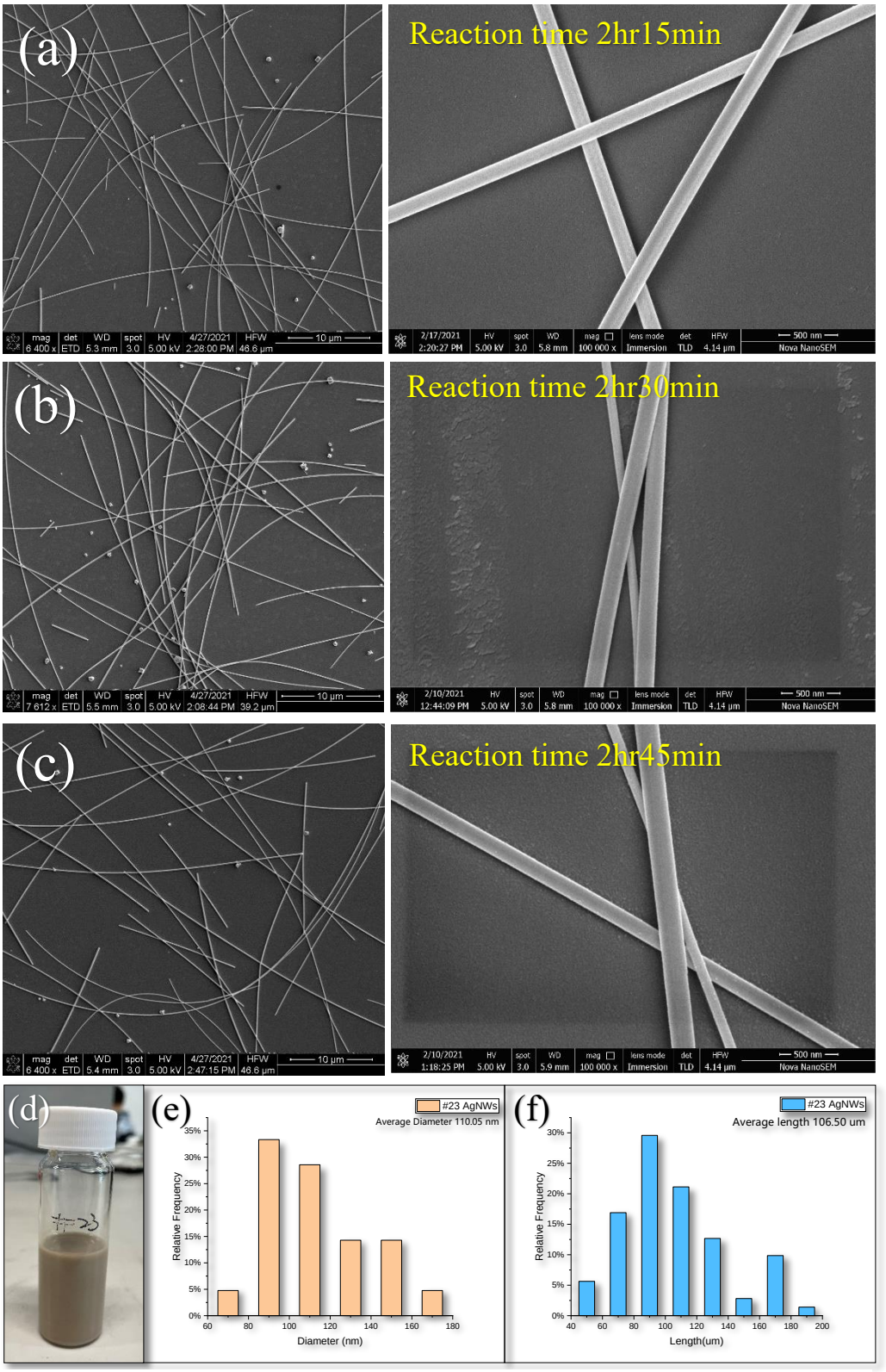

Figure 29 SEM images of AgNWs synthesized with different reaction time (a) 2hr15min (b) 2hr30min (c) 2hr45min; (d) final solution of AgNWs with best aspect ratio and their; corresponding distribution histograms of (e) diameter and (f) length.

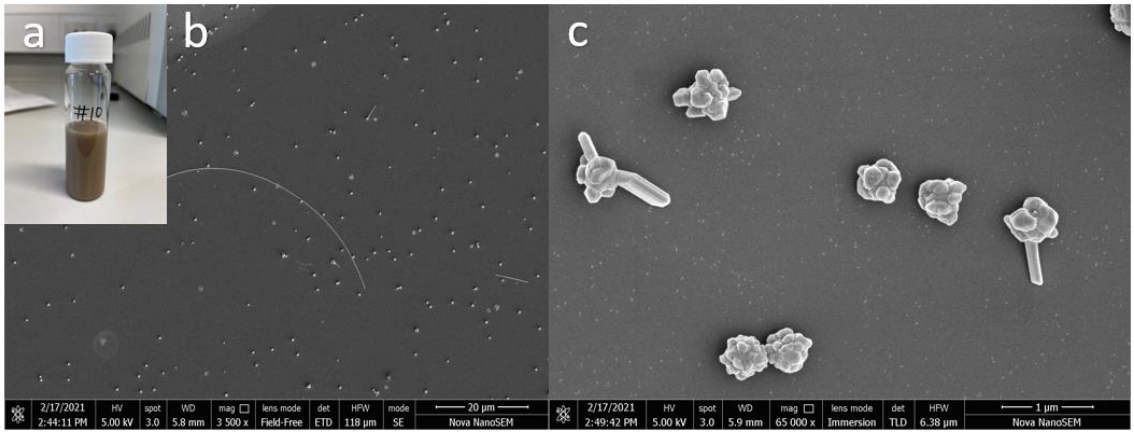

Figure 30 The dark brown-green final solution and (b) SEM images of Maillard-Reaction synthesis reaction time for 2 hr, (c) fresh nanowires emanating from the AgCl surface.

4.3.2 Bromide additive in Maillard-reaction controlled method

It is known that different salt additives could have a big impact on the morphology of silver nanowires. Bromide is one of the primary anions for the enhancement of aspect ratio. From many previous studies, they demonstrated that the diameter would be significantly reduced when adding bromide additives, such as NaBr, KBr, and TBAB[6, 36]. As the diameter of AgNWs we produced through the Maillard-reaction process did not reach our expectation, the NaBr additive was added to see whether the diameter would be reduced and maintain the ultralong length at the same time to enhance the aspect ratio. According to Rui et al.[60], they demonstrated an ETD mechanism for the growth of AgNWs, as I mentioned in section 3.3.2.1. Due to the presence of AgCl and AgBr, they can significantly control the diameter and the length of AgNWs. With the assistance of NaCl/NaBr co-additives, they successfully produced AgNWs with a high aspect ratio of around 2000 when the molar ratio of NaCl to NaBr is 2:1. Therefore, we first synthesized

AgNWs using a 2:1 molar ratio of NH_4Cl/ NaBr via Maillard-reaction controlled process. However, there were almost no AgNWs exist in the final product, and the major products were nanoparticles with the AgCl and AgBr. We then increased the molar ratio of NH_4Cl/ NaBr from 2:1 to 4:1, 10:1, and 40:1 respectively as the high concentration of NaBr could lead to the formation of thick nanowires or even nanoparticles. It seemed like the concentration of bromide was still high when the ratios are 4:1 and 10:1, in which nanoparticles were still main products in the final solution. We obtained about 60% yield AgNWs and 40% nanoparticles when the NH_4Cl/ NaBr molar ratio tuned to 40:1 **(See Figure 31)**. Besides, the diameter of AgNWs has an apparent decrease from 110.05 nm to 87 nm when the molar ratio is controlled at 40:1. Although we successfully synthesized AgNWs through the controlled co-additives, a lot of nanoparticles were also formed, which could alleviate the electrical and optical performance of transparent conductive films based on AgNWs. From the above experiments, we could find that the morphology of AgNWs would be considerably affected by adjusting the concentration of ammonium chloride and sodium bromide. Therefore, we believed that the suitable concentration of co-additives could lead to AgNWs with a high aspect ratio. More experiments and testing are still needed for further understanding of its mechanism.

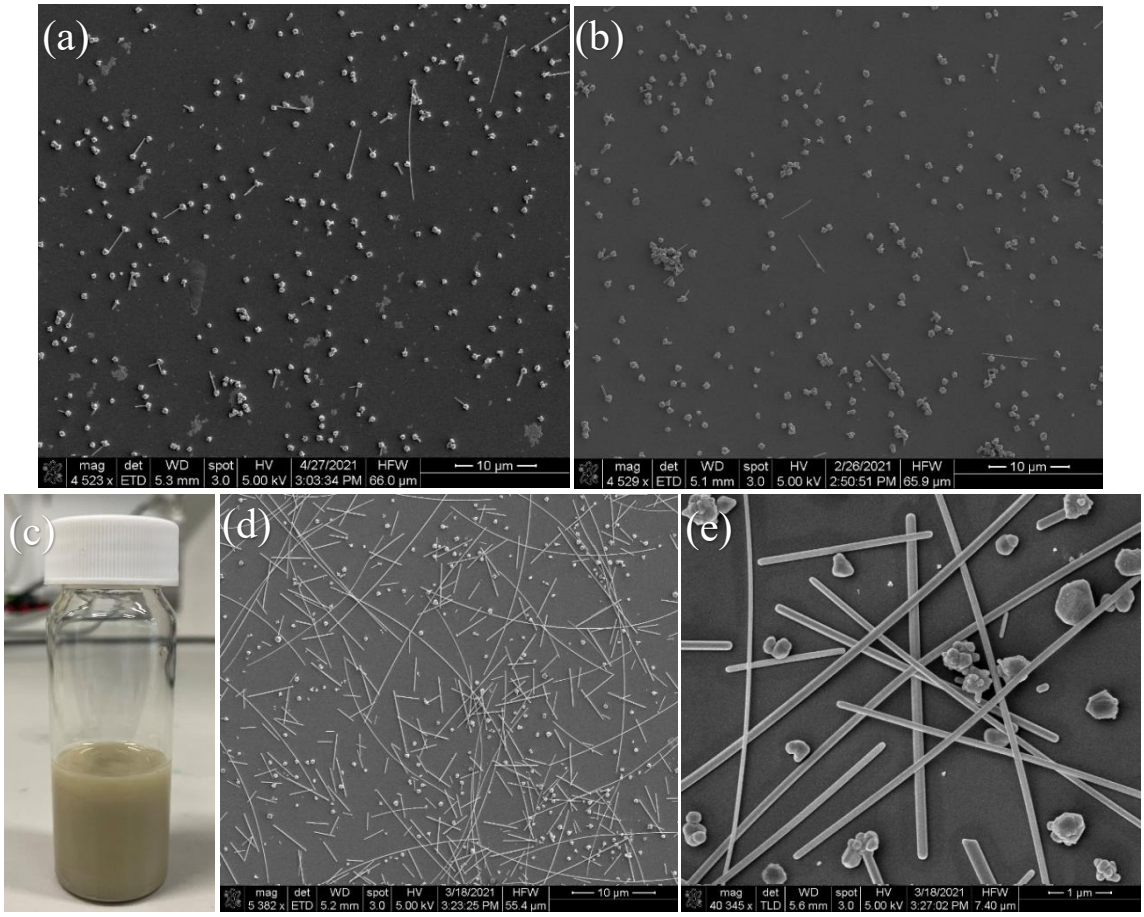

Figure 31 SEM images when the molar ratio of NH_4Cl/ NaBr is at (a) 4:1 (b) 10:1 (d-e) 40:1. (c) the crude solution of (d-e).

4.4 Summary

In summary, plenty of works of tuning the factors, including reaction time, reaction pressure, and the concentration of the additives, were done, and tested. And We successfully produced ultra-long AgNWs with a length of 110 μm through a polyol process by applying a Maillard reaction. Also, we introduced ammonium chloride as one of the Maillard reaction agents into the synthesis, which no other studies used this chemical in the AgNWs synthesis before. From this approach, the Ag-seeds could be

obtained at the low temperature and remain a small size at the early stage. With a suitable amount of additive and reaction time, the ultra-long AgNWs with a length of 110 μm and an aspect ratio of around 1000 were obtained. However, without the autoclave conducted in the synthesis, no AgNWs were observed in the final product, which means pressure from the autoclave in the reaction was a critical factor in producing AgNWs. Moreover, the bromide ion from NaBr was added to the reaction to try to decrease the diameter of Ul-AgNWs. Nevertheless, the results did not reach our expectation after introducing the NaBr in the reaction. We still believe that the diameter could be controlled by bromide ion, but more deep testing and research are needed in the future.[30]

5. Fabrication of transparent conductive films (TCFs) based on silver nanowires

5.1 Introduction

Transparent conductive films have been widely used for many years due to their high transmittance and excellent conductivity, bringing convenience into our lives. TCFs play a vital role in various electronics, including transparent organic light-emitting diodes (OLEDs), transparent film heaters, solar cells, and touch screen devices. The most widely used TCFs material nowadays is Indium Tin Oxide (ITO), which has good conductivity under a high transmittance. However, the technology trend recently is to fabricate flexible electronics which could not make it with ITO. Therefore, many candidates for making flexible TCFs have shown up over the past decades. AgNWs are the most promising option among the alternatives due to their similar ITO properties and remarkable mechanical flexibility. With these properties, AgNWs could maintain their electrical properties under bending and stretching.

In this study, we prepared TCFs based AgNWs via spin coating with several AgNWs samples mentioned in the above section and made the comparison with different parameters. Their electrical, optimal and mechanical abilities are tested in detail here. Also, we introduced some post-treatment to enhance the electrical ability of AgNWs networks in order to improve their performance.

5.2 Fabrication Process

5.2.1 Materials

PET and glass, as-prepared AgNWs solution, Poly-L-lysine solution,0.1% (w/v) in H_2O, absolute ethanol (EtOH). Except for AgNWs solutions, all chemicals were used without any purification and purchased from Sigma-Aldrich.

5.2.2 Fabrication steps of TCFs

Firstly, the glass slides and PET films were cut into square size 25mm × 25mm and cleaned with ultra-sonication in DI water and ethanol for 3 minutes, respectively. Then the glass slides were dried with a nitrogen gun and put into a UV surface processor to do the surface treatment for 15 minutes. The washed AgNWs solution with a concentration of around 0.5mg/mL was prepared. After the surface treatment process finished, 100μL Poly-L-lysine was coated one layer on the surface of each substrate through the spin coating at 3000 rpm for 30 seconds. It is known that Poly-L-lysine could enhance the interaction between AgNWs and the substrate, which improves the electrical property of the conductive film based on AgNWs. When the preparation steps mentioned above were done, the 80 μL as-prepared AgNWs solution was deposited on the substrates by spin-coater at 1500 rpm for 15 seconds as a layer. See the brief fabrication process in **Figure 32**. Afterwards, the transparent conductive films based on AgNWs networks with different layers were fabricated for further post-treatment and electrical, optimal, mechanical testing.

The AgNWs-based TCFs on the glass substrate then underwent thermal annealing post-treatment using an oven. The thermal annealing process was varied from 70 ºC to 250 ºC to the further investigation of TCFs. All as-prepared AgNWs TCFs were measured through ultraviolet-visible spectroscopy (PerkinElmer Lambda 950 UV-Vis Spectrometer). The sheet resistances of the AgNWs-based TCFs were all measured using a four-point probe resistance tester (Kaivo FP-001).

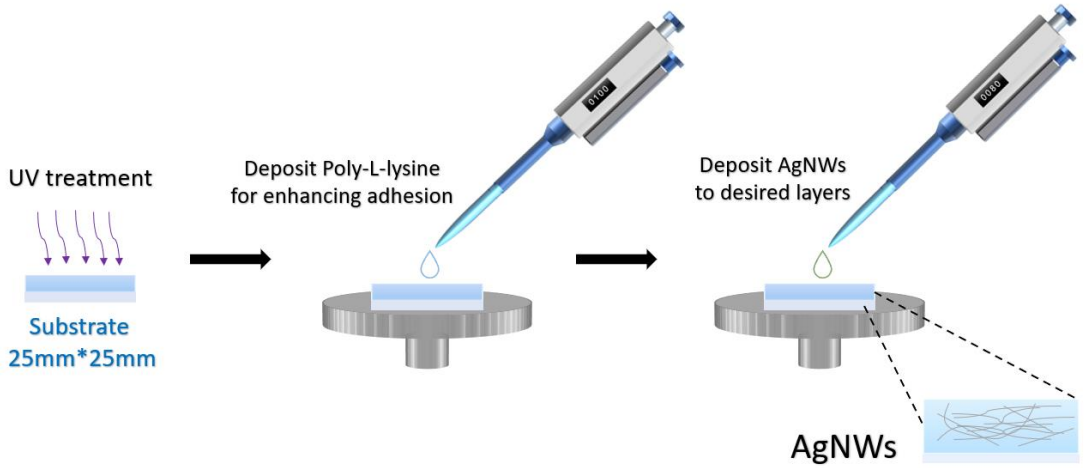

Figure 32 Brief fabrication process of the transparent conductive film based on AgNWs

5.3 Results and discussion

5.3.1 Optical and electrical properties of as-fabricated TCFs

After finishing the preparation of AgNWs-based TCFs, we then tested their electrical and optical properties through a four-point probe and UV-Vis spectrophotometer. Herein, we first took sample whose aspect ratios is larger than 1000 to test the electrical and optical properties. **Figure 34 (a)** shows the sheet resistance with different coating layers on glass using sample S3 mentioned in **Table 6**. The connections between AgNWs play a pivotal

role in enhancing the performance of the networks[66, 67]. It showed that the resistance was high when depositing the first layer, which can be attributed to the non-contacts between nanowires. It is apparent that the transmittance **(Figure 33)** decreased with the increasing coating times, which leads to more interconnections between AgNWs networks. From **Figure 34 (c)**, the sheet resistance decreases dramatically from 0.4784 kΩ/sq (1 layer) to 22.75 Ω/sq (4 layers) and slightly reduced to 5.394 Ω/sq when reached eight layers. (All showed values need to apply the equation $R * 4.517 * 1 * 0.992$ to get the actual sheet resistance).

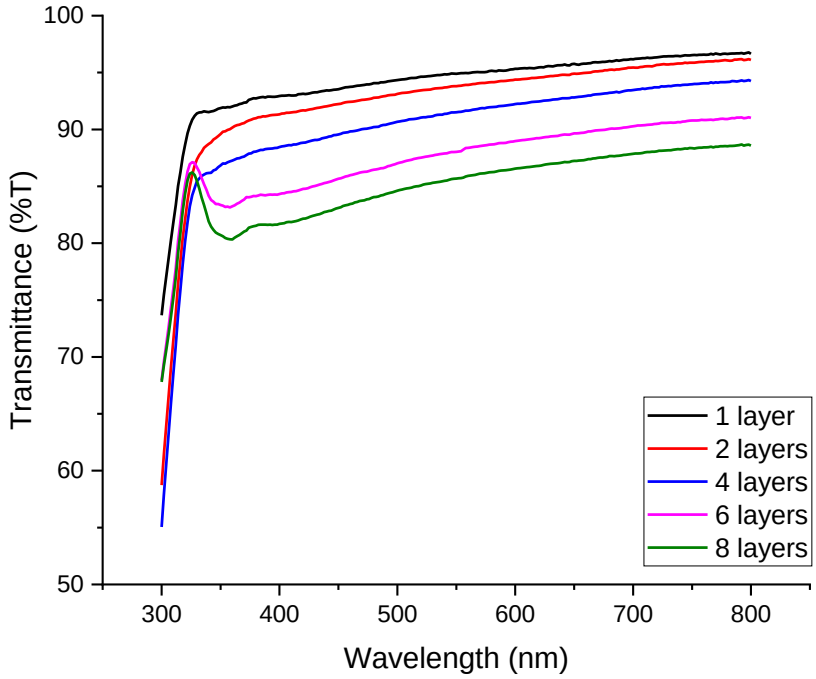

Figure 33 Transmittance spectrum of TCFs with different layers of S3 AgNWs

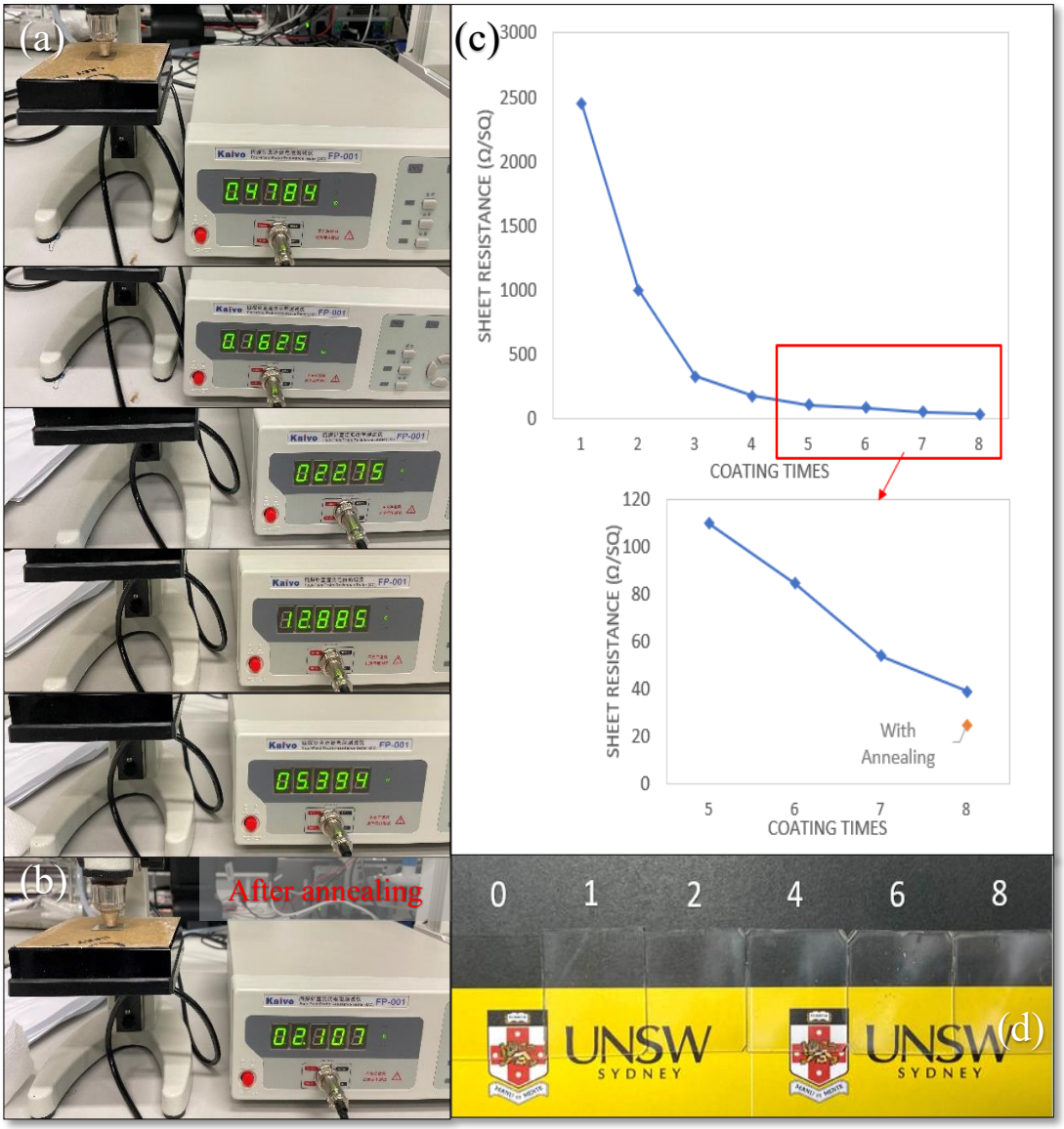

Figure 34 (a) Sheet resistance results of S3-AgNWs based TCFs with different layers (b) Sheet resistance after annealing (c) Variations in the electrical property with different coating times. (d) Haze comparison with different layers

5.3.1.2 Post-treatment of AgNWs-based TCFs

It is known that PVP plays as a capping agent of the synthesis of AgNWs by both two above mentioned methods. The previous works [68] (showed that PVP layer would still attach to the surface of AgNWs, as shown in **Figure 35**. It shows that the PVP is still on the surface of AgNWs with a thickness of about 2 nm. PVP is a vital factor in the synthesis process to limit the growth rate of {1 0 0} planes of AgNW, which determines the formation of a wired shape. However, PVP is an organic chemical that causes the layer of PVP to become an insulating layer. This PVP layer leads the electrical connection and strength of the contacts among AgNWs networks to become weak; therefore, the sheet resistance of AgNWs-based TCFs without any post-treatment significantly increased. The as-prepared TCFs require further post-treatment to enhance the connections between nanowires networks to improve their electrical performance.

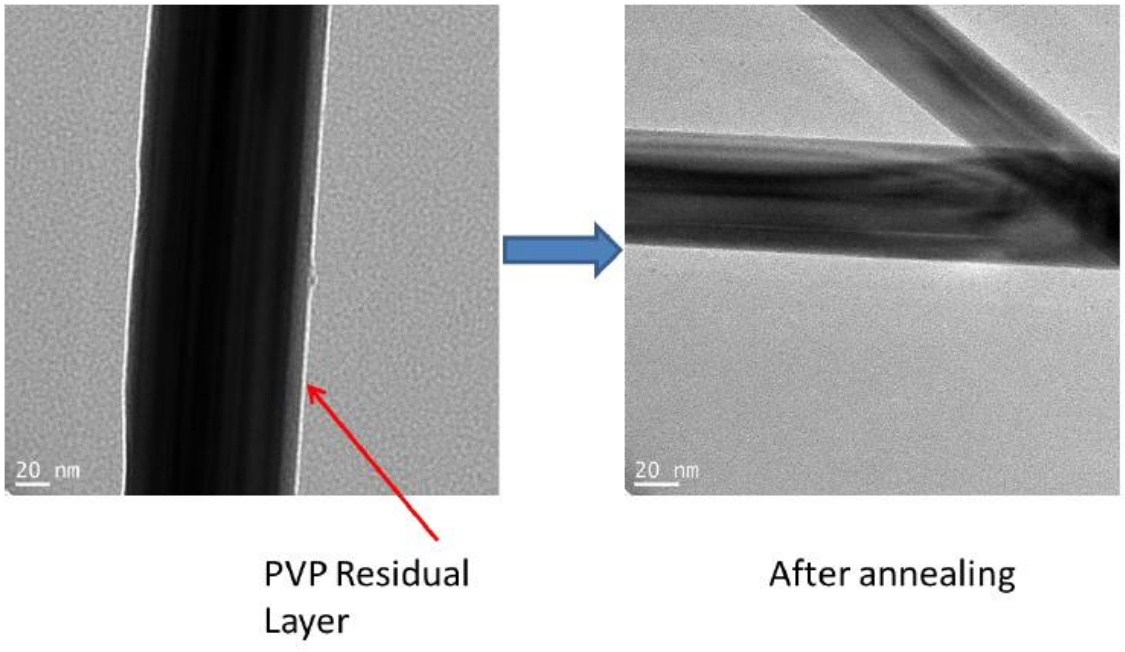

Figure 35 TEM images of PVP layer on AgNWs comparison before and after annealing

In order to show the influence of post-treatment, we chose the AgNWs-based TCF with simple drop-coating using sample S2. All glass substrates were all coated with a layer of Poly-L-lysine and treated with UV light before the AgNWs coating step as mentioned in section 5.2.2. The previous studies reported that the thermal annealing process is an excellent way to eliminate the PVP polymer on the AgNWs surface. In our works, we first tried to do annealing post-treatment at 100 ºC for 20 minutes and found that the sheet resistance decreased from 122.95 Ω/sq to 68.96 Ω/sq (**See Figure 36**).

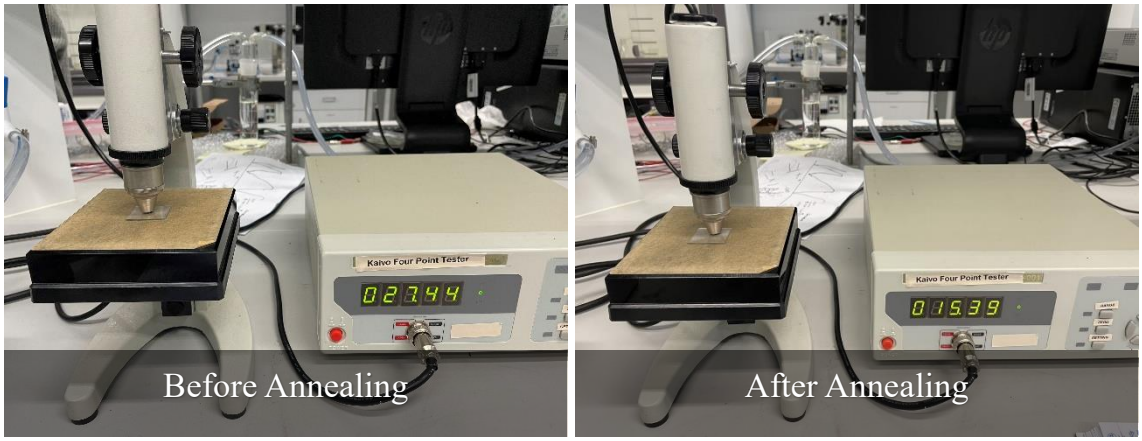

Figure 36 Resistance values from four-point probe before and after annealing

The results demonstrated that the sheet resistance would decrease when applying suitable annealing temperatures. The reason for the decreasing sheet resistance is that because the PVP layer would decompose during the annealing steps, leading to a closer contact between the nanowires. However, it is believed that the formation of AgNWs could cause a considerable decrease in melting point (the melting point of pure Ag is around 962 ºC) due to the increased surface mobility [69]. Here, the eight layers S2 AgNWs coated glass substrate were measured under various thermal annealing temperatures (Room temperature to 250 ºC) to investigate further **Figure 37** shows the sheet resistance of S2 AgNWs TCFs under thermal annealing treatments. From the figure, the results revealed

that with the increase of the temperature from 70 ºC to 130 ºC, the sheet resistance decreased slightly compared to that of the non-annealed TCFs. When the annealing point came to between 140 ºC – 160 ºC, the sheet resistance significantly reduced as the figure shown, and we could get the lowest sheet resistance at around 160 ºC. However, when we kept increasing the annealing temperature from 180 ºC to 250 ºC, the sheet resistance rapidly increased due to the partial decomposition of AgNWs.

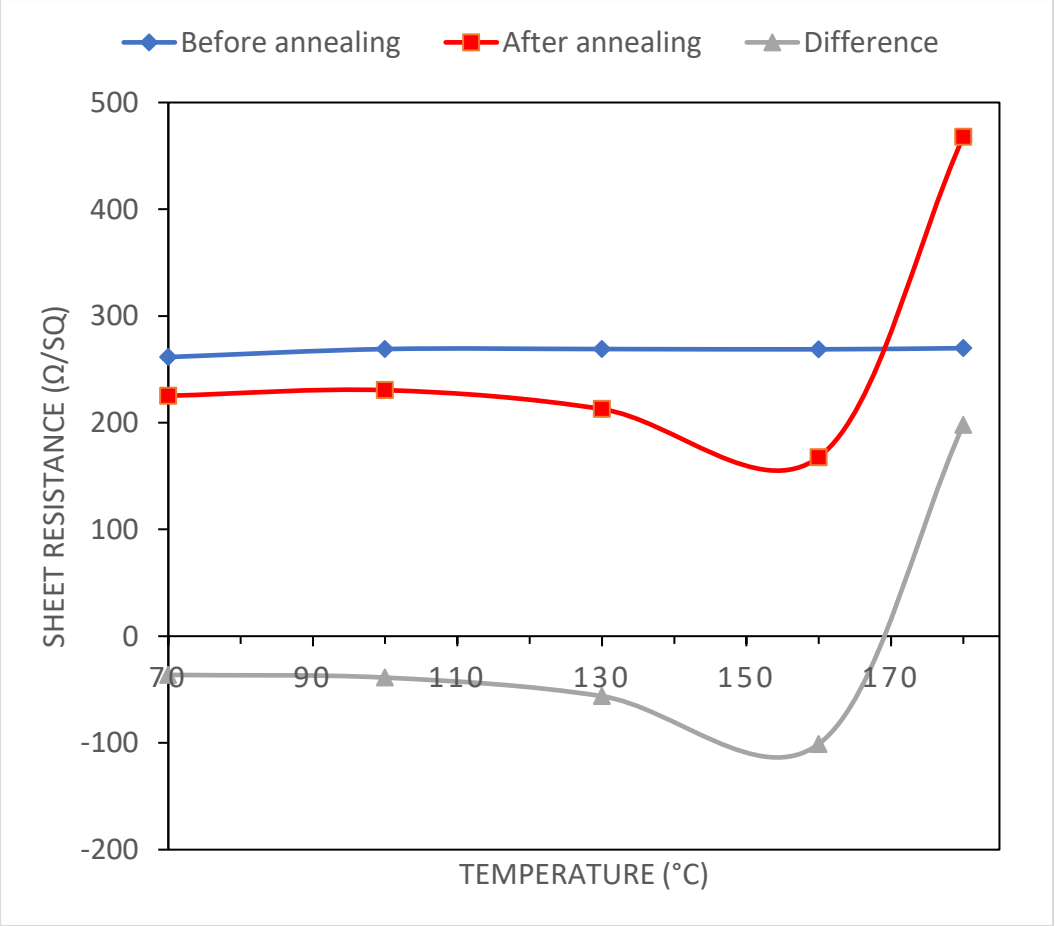

Figure 37 Sheet resistance measurement of S2 AgNWs based TCFs without annealing and with different annealing temperature and the difference.

The SEM images of AgNWs networks on a glass substrate with different annealing temperatures are shown in **Figure 38**. The SEM images confirmed that the connection between AgNWs networks enhanced when the annealing temperature is under 160 ºC. On the other hand, the junction and AgNWs started to disconnect or ruptured after the temperature raised above 160 ºC.

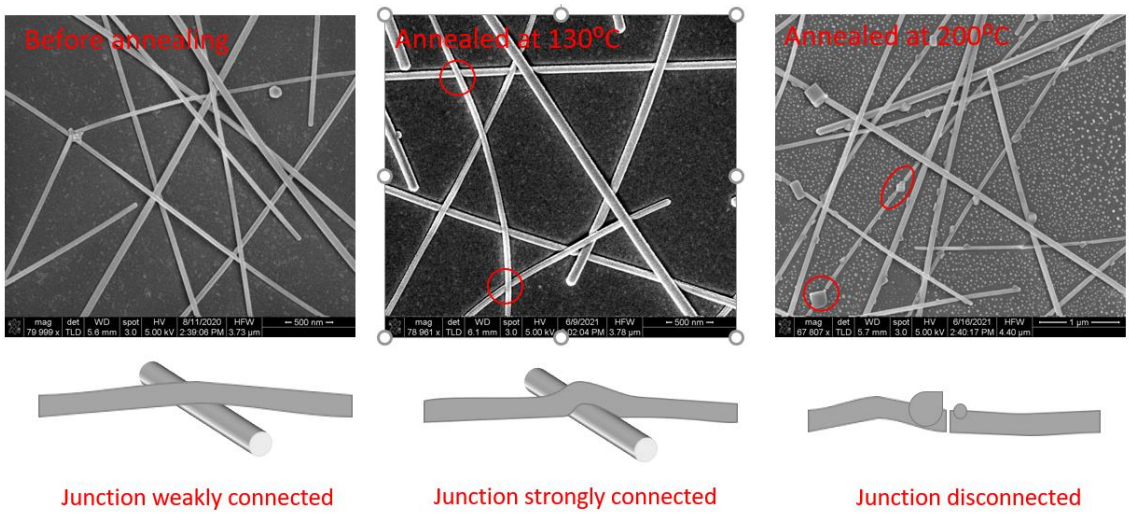

Figure 38 The SEM images of AgNWs coated on a glass substrate before annealing and annealing at different temperatures and schematic diagrams.

Moreover, the optical properties of annealed TCFs at different temperatures (under 160 degrees) were tested using UV-Vis spectroscopy, and the results are in **Figure 39**. As the results from **Figure 39**, the transmittance of S2-AgNWs based TCFs under 70 ºC, 130 ºC and 160 ºC did not have a significant change compared to the non-annealed TCF. Therefore, the results verified that the transmittances could be stable when undertaking the thermal annealing post-treatment and better sheet resistance was obtained simultaneously.

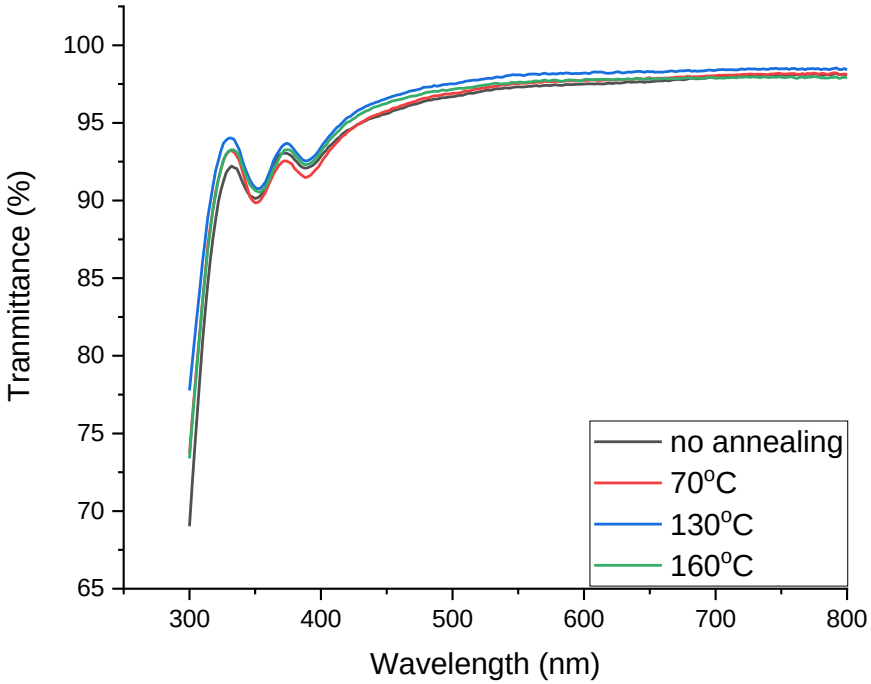

Figure 39 The optical transmittances of non-annealed TCF and annealed TCFs with different temperatures

5.4 Summary

In short summary, the high aspect ratio AgNWs-based TCFs with high transparency (~86%) and great electrical ability (~22 Ω/sq) have been demonstrated in this chapter. The as-prepared AgNWs were successfully deposited on the substrate to build the networks by using spin coating. Plenty of optical and electrical tests of TCFs with different layers of AgNW networks were carried out. It is found that the increasing layers result in low sheet resistance due to the expanding junction contact; however, it decreased the optical transmission. To improve the electrical properties, we employed thermal annealing post-treatment for 20 min after the coating process. The results pointed out that the sheet resistance decreased gradually when the temperature increased from 50 ºC -160

ºC. The best electrical property could be obtained when conducting the annealing post-treatment at around 160 ºC. Yet, the sheet resistance increased sharply when the temperature was above 160 ºC due to the crack between AgNWs networks. Besides, the transparency did not have a significant change after conducting the annealing post-treatment.

6. AgNWs based electrode for electro-chemical syngas production from Carbon Dioxide

6.1 Introduction

The global warming and climate change have been hot topics in recent years. The largest driver of these problems is the human-induced emission of greenhouse gases, in which the major proportion are carbon dioxide. To diminish the greenhouse effect, researchers have been focused on developing the method to convert CO_2 to high-value fuels efficiently. Synthesis gas (Syngas) is fuel gas mixture consisting primarily of carbon monoxide (CO) and hydrogen, which can be used to generate synthetic natural gas, ammonia, or methanol. Coal gasification is a major product from syngas and the main application is electricity generation. However, syngas is traditionally produced from water-gas shift reaction, which is high-energy consumption and could cause some environmental issues. Therefore, it is highly needed a new way to efficiently convert carbon dioxide to syngas.

Many metals have been selected for converting CO_2 into CO-rich syngas, especially Au, Pt, and Ag in previous studies. Ag is considered as one of the most attractive material among these metals due to its excellent stability and lower cost. Therefore, there are various types of silver, including polycrystalline silver, Ag plate, 3D porous Ag, and Ag nanoparticles, have been researched for electro-chemical reduction of CO_2 [70-72]. Although some of the studies could reach the high syngas transformation, there are still some limitations, such as the high costs and the low active sites. It is believed that the nanostructure of silver could provide more active sites than bulk silver and leads to the

higher CO_2 reduction Faradic efficiency (FE). Nevertheless, there are few studies and experimental research on the metal nanowires, which may have a high potential of making CO_2 electrochemical reduction in an effective way. Herein, the AgNWs with aspect ratio about 1000 were used for syngas preparation from CO_2.

6.2 Preparation

The as-prepared Ag nanowire ink (S3) was mixed with 5% wt. Nafion solution for drop-casting on carbon fiber paper (loading amount of 0.5 mg/cm^2) and dried at 110 ºC for following electrochemical test.

6.3 Result and discussion

In the previous study from Xi et al.[73], they demonstrated the catalyst performance of Ag plate, AgNPs and AgNWs which showed that the AgNWs electrode has a high selectivity of converting CO_2 to CO. This revealed that the AgNWs based electrode is a promising material of generating syngas of CO_2. Herein, the electrochemical CO_2 reduction experiment of the AgNWs (S3) based catalyst was measured in H-cell filled with 0.1 M $KHCO_3$ saturated with CO_2 under the different applied potential range of -0.6 to -1.4 V vs. RHE. According to Liu et al., the research showed that the 5-fold twinned nanostructure of AgNWs leads to a better stability than AgNPs due to its abundance corners and edges as the active sites [54]. As shown in **Figure 40**, the current density was stable during the 1.5 h CO_2 reduction experiment, indicating the good stability of the AgNWs catalyst under reaction conditions.

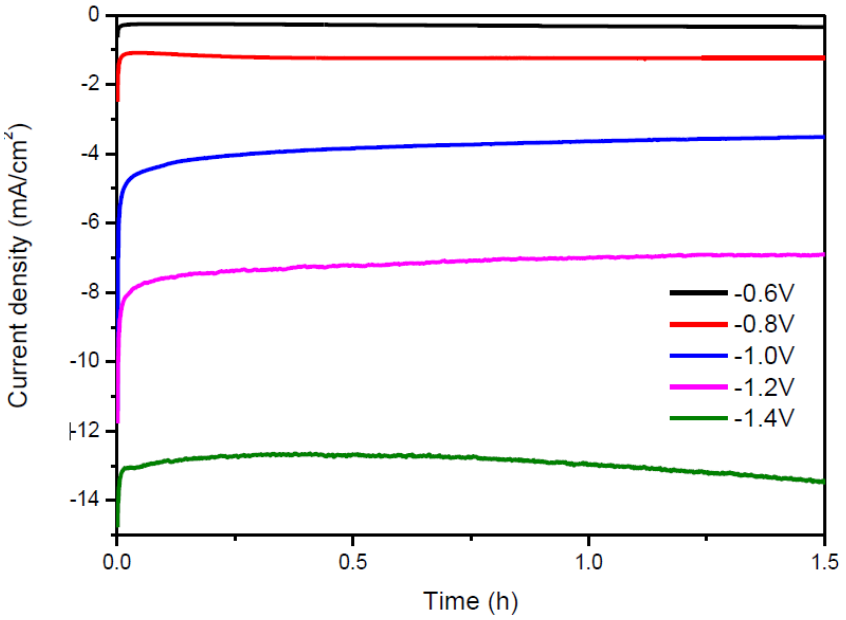

Figure 40 Current density of Ag nanowire catalyst in H-cell filled with 0.1 M $KHCO_3$ saturated with CO_2 under different applied potential.

The total current density and CO_2 reduction partial current density is shown in **Figure 41** shows that the Ag catalyst started to produce CO_2 reduction products at around -0.8 V vs. RHE. In comparison, the HER reaction became more competitive at more negative applied potential than -1.2 V vs. RHE. The product distribution shown in **Figure 42** revealed that the catalyst is able to reduce CO_2 to CO and a small amount of formic acid, and CO was found to be a leading product from CO_2 (peak faradaic efficiency of ~28%). H_2 was also be detected which generated form H_2O. The percentage of Faradic efficiency is the key index to observe the efficiency of charged electron are transferred during the conversion of CO_2 to CO and other formic acid. **Figure 42** revealed the maximum Faradic efficiency of CO_2 conversion is about 30% under -1.0 V (vs. RHE) and will decrease with the increase of applied potential for AgNWs catalysts. The H_2 FE percentage remained stable at around 75% and a little amount of formate started to be generated when applied potential was at -1.0 V.

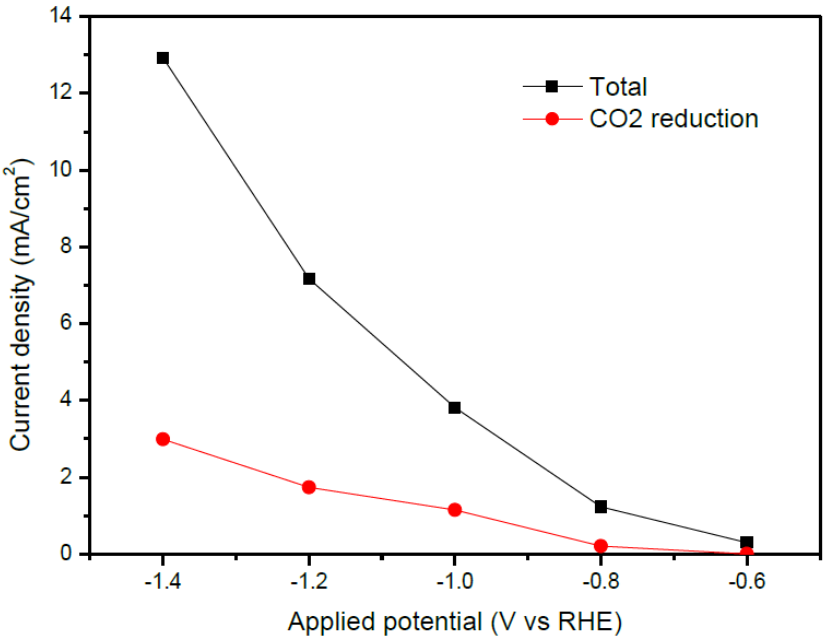

Figure 41 Partial current density towards CO_2 reduction products of Ag nanowire catalyst in H-cell filled with 0.1 M $KHCO_3$ saturated with CO_2 under different applied potential.

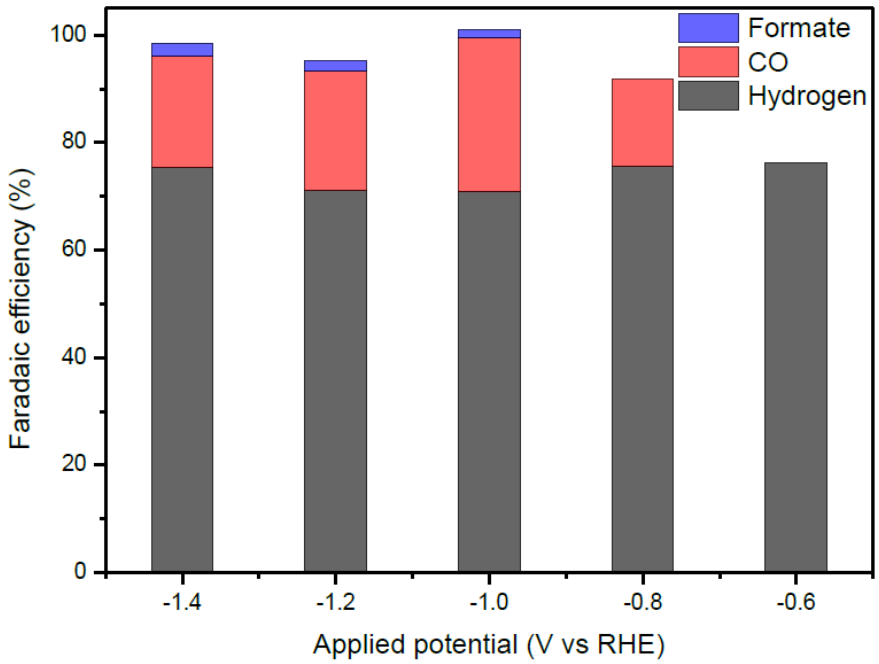

Figure 42 CO_2 reduction faradaic efficiency of Ag nanowire catalyst in H-cell filled with 0.1 M $KHCO_3$ saturated with CO_2 under different applied potential.

As more than 90% of the products are CO and H_2, it is worthwhile to investigate further the properties of Ag catalyst for producing syngas. For future investigation, we could change the preparation parameters of the Ag catalyst to tune the CO/H_2 ratio in the syngas product. According to the study by Liu et al.[54], they verified that the catalytic activity could be improved due to the increased ratio of active sites contributed by the diameter and length effects. Besides, the networks of AgNWs provide many pores, which gives assistance to the transformation of CO_2, and capability of the reduction is enhanced as well. There are many of factors may influence the reduction of CO_2, such as facet, impurities, mass of AgNWs and morphology. The previous experimental works revealed that the edge/ corner ratio is favorable for the conversion of CO_2 to CO and the plane {111} of Ag showed the most stable activity among other facets [74]. Therefore, the different formations of pure AgNWs might bring the significant improvement to the CO_2 conversion rate.

6.4 Summary

In conclusion, the results indicated that AgNWs-based electrode could convert CO_2 to the syngas (CO and formate) and the main product of syngas was CO. However, the performance of electro-chemical reduction of CO_2 using AgNWs based electrode did not reach our expectation due to the low CO_2 conversion rate. According to previous study[53, 54], it is believed that the thinner AgNWs could enhance the Faradic efficiency and a lower potential for high selective reduction of CO_2 to CO. Various tests with different parameters and experimental environments are needed in the future investigation to find a best way and condition to improve the performance.

7. Conclusion and prospects

7.1 Conclusion

This work found that the high aspect ratio AgNWs could significantly enhance the electrical and optical performance of AgNW-based TCFs. Therefore, two different synthesis methods of AgNWs have been systematically investigated to produce AgNWs with a better aspect ratio (>2000). For the solvothermal process. The 90 ºC was found to be the suitable temperature to control the formation of AgNWs and the PVP dissolution rate. Besides, when the molar ratio of PVP to $AgNO_3$ and MW of PVP controlled at 9.45:1 and 1300000, respectively, the AgNWs with the highest aspect ratio of ~2000 in this project were obtained. The results pointed that the longer chain of PVP significantly affects the formation of PVP, especially their lengths. Moreover, two critical ionic additives (NaCl & NaBr) were used to control the formation of AgNWs and different morphologies were observed by varying the molar ratio of dual additives. The AgNWs with the aspect ratio ranging from 350 - 2000 were obtained via the solvothermal process when changing the various parameters.

For the Maillard reaction- controlled synthesis, with the help of MRPs, they can control the reduction kinetics and affect the sizes of silver seeds at the early stage. Herein, the ammonium chloride which has never been used before and glucose were used as the Maillard-reaction agents. The uniform AgNWs with aspect ratio of about 900 were obtained when only one salt additive (NH_4Cl) was added during the 2 hr 30 min reaction. In addition, it was hard to produce AgNWs when adding the extra bromide additive into the reaction and without using an autoclave.

Second, the AgNW-based TCFs were fabricated to measure the electrical, optical, and mechanical properties. It was found that if the temperature of heat-treatment is above 160 ºC, the sheet resistance of TCFs would drastically increase due to the crack of AgNWs. With the suitable time and temperature of annealing post-treatment, the S3 AgNW-based (AR ~1000) TCF with high transparency (86%) and low sheet resistance (~22 Ω/sq) was obtained.

Third, the AgNW-based transparent conductive electrodes have the potential for electrochemical syngas production from carbon dioxide. Herein, the S3 AgNWs-based electrode was used for the electrochemical measurement. The results revealed that the silver nanowires electrode successfully converts CO_2 to the syngas via electrochemical reduction measurement and has high stability. However, the Faradic efficiency of syngas only reached ~30% when the applied potential at -1.0 V (vs. RHE), and the performance did not achieve the expectation. Many factors cause the poor performance, such as the formation of AgNWs or the amount of usage of AgNWs. Thus, further investigation of optimizing the performance through tuning the parameters is needed in the future.

7.2 Prospect

Advanced nanomaterial electronics have been researched and studied recently. Fabrication of wearable/ flexible electronic devices has been a trend in recent years as the demand for these devices will become huge in the future. Thus, AgNWs have become the most promising material of developing these flexible electronic applications among various candidates due to their excellent electrical, optical, and mechanical properties. It

is known that thin AgNWs with a high aspect ratio can have outstanding performance in those properties as mentioned above. To enhance the performance of AgNW and control the morphology of AgNWs, tuning different parameters, including the reaction agents, temperature, or molar ratio of co-additives, are still necessary via the most common synthesis (polyol synthesis) to control the morphology of AgNWs. Besides, the latest synthesis methods Maillard reaction process is expected to develop a cost-efficient way of generating AgNWs. It has a great potential of making silver nanowires in thin diameter due to its strong reduction ability at the initial stage. Yet, many factors in this method are still unclear, especially the mechanism between the glucose and the ammonium compounds and the stability. Therefore, more studies of this Maillard reaction process are required in the future. In summary, with more research on the polyol method and Maillard reaction process, it is believed that they will contribute to the development of AgNW-based wearable devices and advanced electronics.

For the fabrication methods, printing techniques, such as inject printing and EHD, are the next-generation coating methods of fabricating the transparent conductive film. It is a simple way to coat the special pattern networks via printing techniques to fulfill the different demands of certain electronics. Producing the pure and uniform AgNWs ink for printing is crucial due to the specific nozzle size of the printing devices. Finding a way to prepare the ink with uniform AgNWs and no impurities can optimize the printing performance.

Environmental awareness has been increased recently. Many studies related to reducing and recycling greenhouse gases have been carried out. AgNWs are candidates, which have a great potential of converting carbon dioxide to high-value gasses (Syngas) through

electrochemical measurement due to their remarkable stability and electrical property. For future research, AgNWs with different diameters or other metal materials can be employed to enhance the performance of syngas production.

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