

The Development and Application of Silver Nanowires as Flexible Transparent Electrodes

Yuhang Li *

School of Materials and Engineering, Northeastern University, Shenyang, 110167, China

* Corresponding author's e-mail: 20193395@stu.neu.edu.cn

Abstract. Throughout the past 100 years, the electronics industry has developed rapidly. Research in the field of electronics is becoming more and more thorough. As a transparent conductive oxide (TCO), indium tin oxide (ITO) has dominated the flexible transparent electrode market since 1970. However, due to its limited production, high cost, and inflexibility, these limitations hinder the further development of ITO, so this paper turns the attention to the substitutes of ITO materials, such as silver nanowire AgNW and carbon nanotube CNT graphene. Because AgNW has good synthesis scalability and reproducibility, they can be easily dispersed in solvents, which is related to low cost and low cost. It consumes fewer raw materials than ITO and has similar optoelectronic properties. The produced AgNW electrode has high electrical and thermal conductivity, high optical transparency, and flexibility, which attracts people's attention. Therefore, this paper focuses on the preparation, performance improvement, future application, and development prospect of silver nanowire AgNW electrode.

Keywords: Flexible transparent electrodes, silver nanowire, carbon nanotube, ITO materials.

1. Introduction

The field of the electronic industry has developed rapidly in the past hundred years. As seen in Fig. 1, there has been a sharp increase in electronics-related literature and Scopus publications [1].

Through the analysis of this chart, this paper concludes that in the early 1940s, the development speed of electronic products was unmatched by other industries. In the 1940s, the publishing speed of related papers in the electronic industry exceeded 1100%. The rapid development of related materials is the key point. Now take the development of semiconductor material Si as an example, its development speed is far beyond people's imagination, which greatly promotes the development of electronic materials. Si-related chips have impacted the development of the electronic industry [1]. The rapid development of semiconductor materials related to silicon is the reason for the development of the electronic industry. Thus, in the 1950s and 1960s, the field of science and technology related to chip electronics developed rapidly, growing at a rate of 3,300%. Even in 1964, Moore put forward the famous Moore's Law, that is, the number of transistors that can be accommodated in an integrated circuit will double every 18 months [10]. This is Moore's experience as an insider. The improvement of the performance of si-based semiconductors has promoted the development of the whole field of electronic products, but now si-based materials will soon be restricted, so it is an urgent problem to develop new materials that can replace Si-based materials [7]. Among them, the most common and classic indium tin oxide (ITO) is used as a flexible transparent electrode in electronic screens and new energy renewable batteries, which has an irreplaceable position with products.

Electronic products should be light, flexible, bendable, and stretchable enough to conform to the body movement to be more closely combined with the human body and pursue comfort [20,21]. Among them, AgNWs, a representative one, has attracted much attention because of their good electronic material performance, which also attracts everyone's attention. The excellent performance of AgNWs is not limited to the excellent thermal conductivity and electrical conductivity but also has good transparency, thermal performance, and excellent properties in the mechanical field [4]. It can operate in solution to a large extent and has electrical properties that other materials can't match. Using AgNWs as a conductor in some foldable, flexible electronics elements will get nearly 80% light transmission effect. In some references, AgNWs can even achieve a similar effect with ITO [1]

This paper will detail how to improve the manufacturing quality and large-scale production of silver nanowire flexible transparent electrodes. It provides a solution to produce the silver nanowire flexible transparent electrodes on large scales with uneven conductivity, rough surfaces. Compared with the practical application, this review focuses on improving silver nanowires' preparation method to construct flexible transparent electrodes.

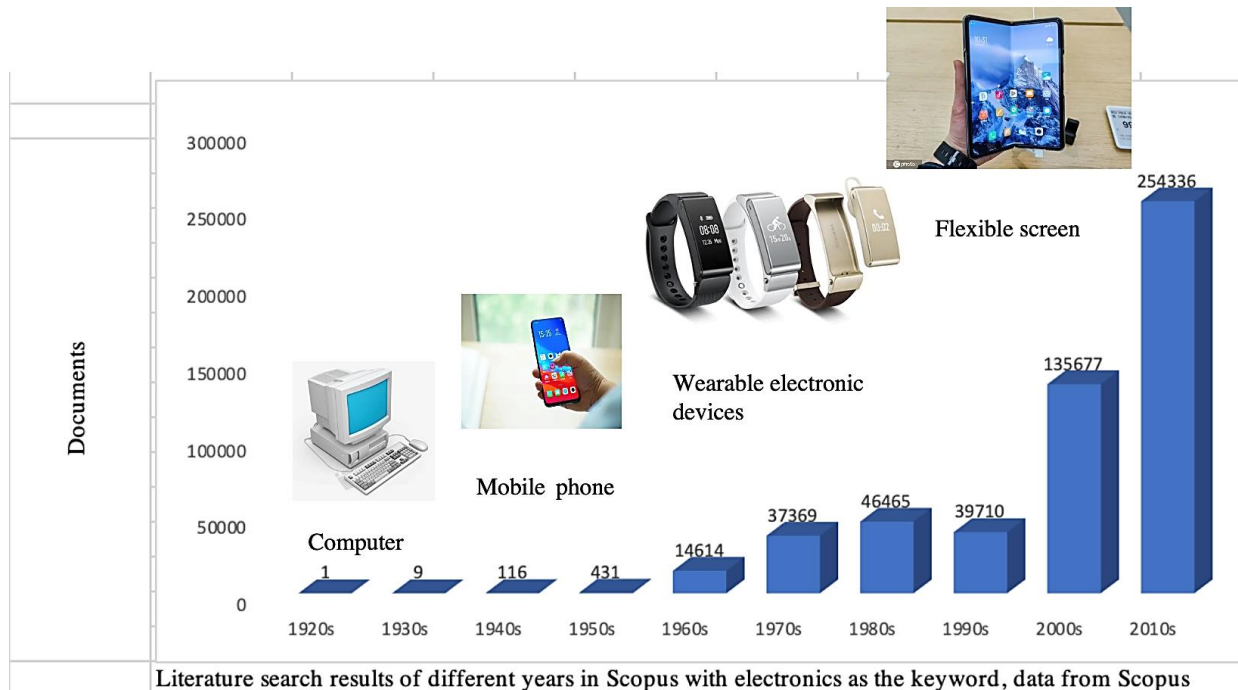


Figure 1. Development of Electronic Literature

2. The manufacture of flexible transparent electrodes with silver nanowires

Silver nanowire is a kind of nano-scale wire called silver nanowire because its material is silver. To Figure 2, silver nanowires are one-dimensional nanomaterials. Because of their excellent photoelectric properties and bendable mechanical properties, silver nanowires are also considered the most promising substitutes for indium tin oxide.

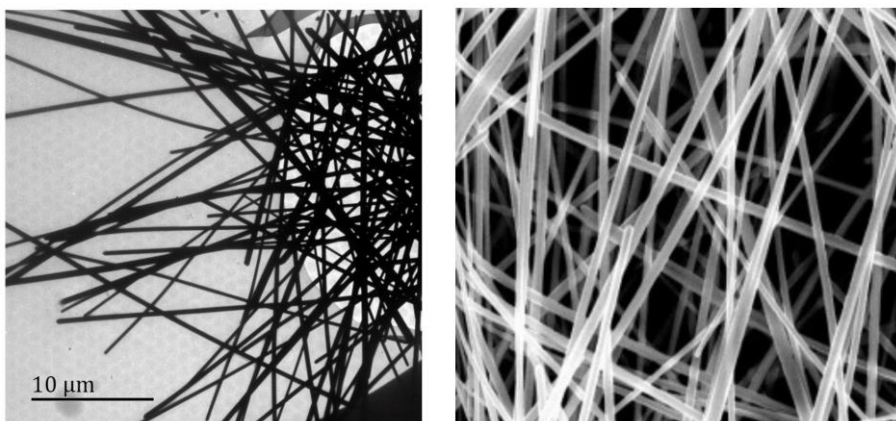


Figure 2. Characterization diagram of silver nanowires

2.1. Method for obtaining AgNW flexible transparent electrode Coating method:

Silver nanowires come in wide different varieties. The transparent electrodes of silver nanowires must be sealed off from the air to prevent the reaction. They are built on an organic polymer substrate made of polyethylene terephthalate (PET) and covered in an organic polymer material (Teflon with a thickness of 20 nanometers). The specific production process will be covered in more depth below.

2.1.1. Spin Coating

Disperse the prepared AgNW in an organic solvent with high solubility and make an AgNW-based conductive film in the solution. AgNW will create a network of conductive paths on the substrate. However, the thickness, homogeneity, conductivity, and transparency of the generated AgNW sheet cannot be controlled. There are several ways to address these issues at the moment. Let's use the Spin coating approach as an illustration to address this issue. The usual method for making membranes in the lab is spin coating. Spin coating is the method of using centrifugal force to create an even layer on a rotating surface. The film is left behind when the volatile solvent evaporates during the rotation operation. The biggest convenience of this method is that it can produce the required film with the standard in thickness and size in a short time. But at the same time, the loss of raw materials caused by rotation cannot be ignored, which is why it is difficult to put into mass production.

However, by improving this technology, researchers such as Lee applied AgNWs to the surface of graphene prepared in advance by spin coating technology, which improved the surface of graphene in the fields of thermal and electrical conductivity. The AgNWs can be the connecting medium [Figure 3.a, b]. Lang et al. also used spin coating technology to prepare the required transparent and conductive flexible film [5] so that organic-inorganic hybrid organisms in the polar state and organic-inorganic hybrid organisms in a nonpolar state can be produced. The obtained product can be fully contacted with AgNWs, and the combined AgNWs can be rotated at different speeds (from 300 to 5000 rpm). It can use this special method to achieve the standard requirements in thickness.

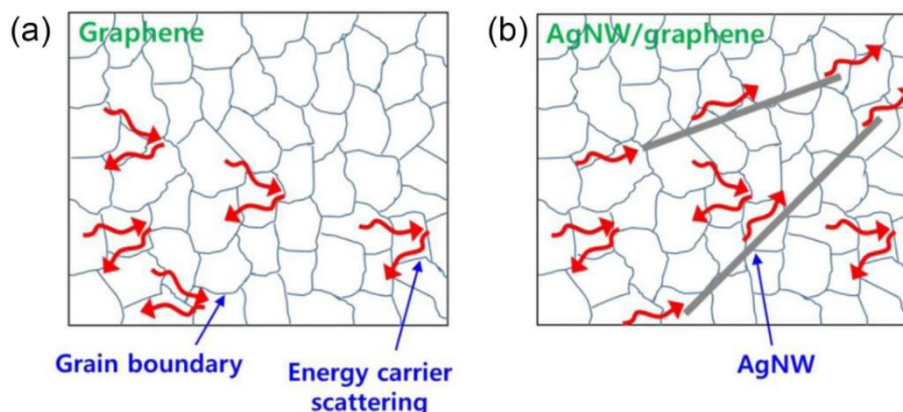


Figure 3. The illustration of power transmission in films of: (a) Polycrystalline graphene; (b) AgNW graphene.

2.1.2. Meyer rod coating

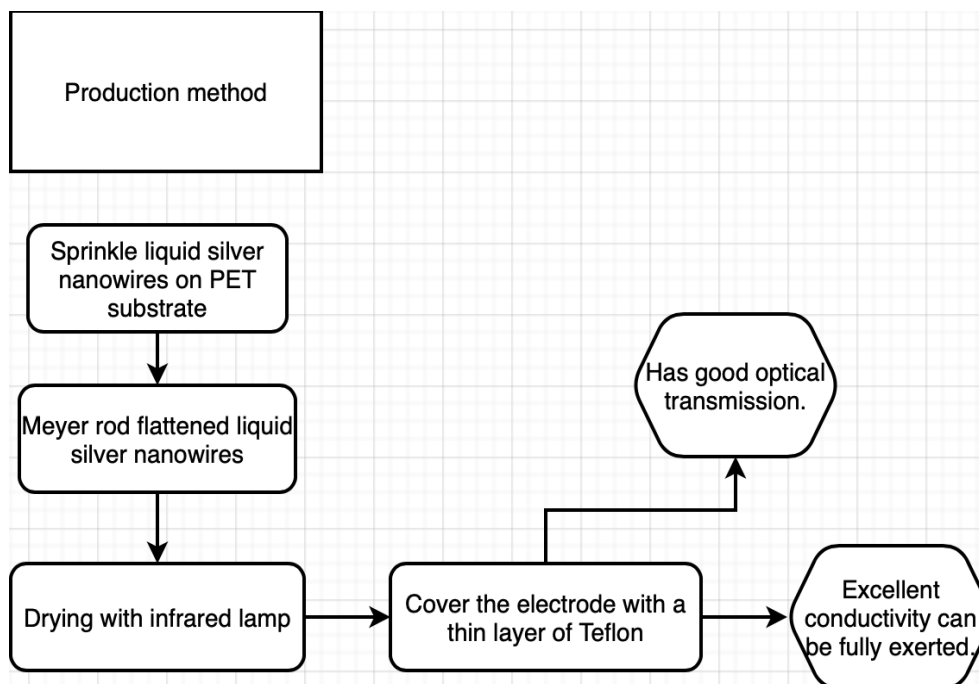


Figure 4. Flow chart of making flexible transparent silver nanowire film by Meyer rod method

In this review, the author gave us a method of fabricating a foldable flexible electrode with high transparency at the optical level by Meyer rod method (Figure 5.b). Next is the process in detail: the researchers used scientific and technological methods to make the prepared silver nanowires in liquid state fall on (polyethylene terephthalate) PET substrate relatively evenly, and then used Meyer rod to flatten it evenly. This process can enable us to obtain silver nanowires with approximately the required thickness, which is also of great help to improve the performance of the motor in the conductive direction and the photoelectric transmission direction. Then, it uses infrared spotlight to dry it optimally. Through this step, it can form the prepared organic polymer into the silver nanowires on its substrate (Figure 5.c). As the silver nanowire flexible transparent electrode constructed in this paper is easy to react with other substances in the air, a layer of polytetrafluoroethylene with a thickness of about 20 nm is covered on the surface of the prepared silver nanowire film to protect the flexible transparent electrode material prepared by us. The electrode made of this material will show excellent conductivity and good light transmission performance.

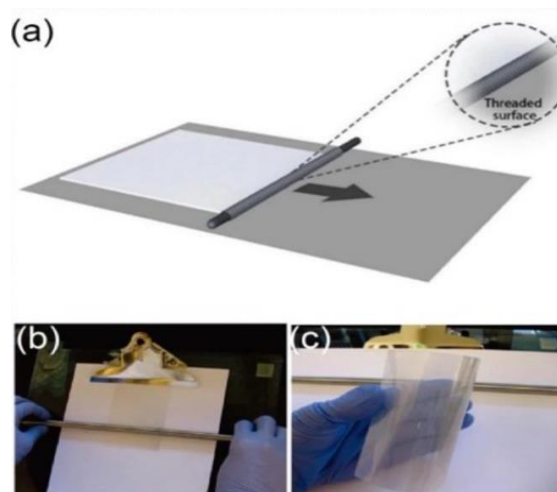


Figure 5. (a)Diagrammatic representation of the Meyer rod coating manufacturing process, (b)Real flowchart of the Meyer rod coating manufacturing process, (c)On the PET substrates, AgNWs were consistently formed [6] [15].

However, the silver nanowire film produced by the above method will have a big defect. The large-area silver nanowire conductive film produced will have a serious consequence of uneven conductivity of the conductive film due to uneven thickness. Thanks to the dynamic heating mode instead of the traditional fixed heating mode, researchers have fully improved the uniformity of the silver nanowire conductive film. Instead of fixing the silver nanowire conductive film, the film was repeatedly moved at a slow speed of 0.05 meters per second under a xenon lamp. Dynamic heating will make the temperature gradient more uniform than the traditional heating method. This method successfully avoids the uneven conductivity caused by xenon lamp heating in fixed position.

2.1.3. Electrical conductivity

Since the AgNW electrode plate's resistance is made up of a single nanowire, The distribution of silver nanowires on the required substrate, and the other materials in the immediate vicinity impact the connection between wires. A single nanowire's length, size distribution, and diameter are all properties influenced by unique variables. A longer nanowire film requires fewer wires to pass through a specific space, thus reducing resistance. Although it is believed that the number of connections between silver nanowires controls the length of silver nanowires, the actual situation is not so simple, and the number will change due to the different extension directions of silver nanowires. At the same time, different production methods will lead to different contact patterns between wires, which will have a direct or indirect impact on the resistance. The initial junction resistance is much higher than that of a single nanowire. However, different follow-up treatments can reduce it by several orders of magnitude. However, the investigation by researchers shows that by limiting the junction resistance to zero, the sheet resistance of the film can only be reduced by about 20%. This paper can further improve the conductivity by increasing the width ratio to the height of nanowires and developing new configurations of nanowires at the geometric level, which should reduce the resistance of individual nanowires. The density of AgNW nanowires will also affect this. Increasing its density above the percolation threshold will lead to a decrease in accurately control thickness to produce resistance. The resistance of the resistor decreases with the increase of the density of the nanowire.

2.1.4. Optical transparency

In addition to the electrical conductivity, to consider silver nanowires' optical transparency when choosing them. In these practical applications, it can be found that the extinction region is the smallest in the visible light region, but at the same time, it can keep a high conductivity. Figure 6 (a) demonstrates a blueshift of the transverse plasmon resonance and a narrowing of the peak when the wire's radius is reduced. Thinner nanowires must be created in order to be used in transparent electrodes, and this blueshift toward the UV part of the spectrum has been cited as evidence [18]. This strategy is correct, as can be seen in Figure 6. (b), which depicts the example of a transmission network (λ) before (black) and after (blue) the solar spectrum multiplied by the sensitivity of human eyes, and AgNW network, the blue shift of extinction is only a few nanometers. With the decrease of the radius of nanowires, the maximum transparency gain is due to the decrease of the geometric size of nanowires, resulting in lower residual extinction above 500 nm.

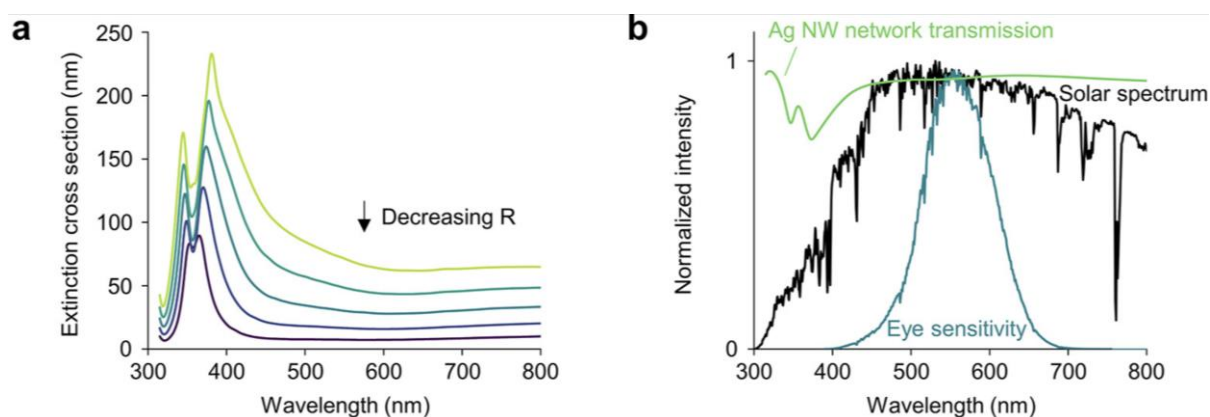


Figure 6. AgNWs for transparent electrodes.

The sheet resistance of the AgNW network is influenced by the resistance at each NW intersection as well as the resistance between connection points. The network's sheet resistance only depends on the number of junctions when the junctions' conductivity is low [19]. The inverse proportional relationship (Figure 6a) shows the infinite pentagonal conductor's image in the extinction cross section field. In the process of gradually reducing the radius from 35nm to 15nm in the case of 5nm steps, the number of junctions is not changed by the change of curvature radius $R_{\text{curv}} = 10 \text{ nm}$, so it will not affect the resistance of the thin layer with controlled thickness, which will make this design much easier. However, the use environment of the AgNWs network has been subjected to mechanical pressing treatment after deposition for a long time [7] or heat treatment [6]. By reducing the junction resistance, the internal wire resistance can be made as low as possible, making it impossible to ignore this data set. A small radius is desired for very transparent networks. In contrast, a large radius is chosen for highly conductive networks since the resistance of a single wire is inversely proportional to its cross-sectional area.

2.2. Improvement of photoelectric performance of AgNW flexible transparent electrode

Photoelectric performance is the most critical performance of flexible transparent electrodes and the most advantageous performance of AgNW material. According to the permeation theory, the size of AgNW is directly proportional to the performance of the flexible transparent electrode formed by AgNW. A longer AgNW can provide better electrical conductivity and achieve a balance between good electrical conductivity and excellent optical transparency, our prerequisite is that the optical transparency should not be reduced, so as to improve the optical and electrical properties of flexible transparent electrodes of AgNWs. Nowadays, the most effective and widely spread way to synthesize AgNWs is polyol synthesis. Jiu et al. [6] controlled polyol by adjusting the stirring speed of AgNWs. This method has been partially successful, and this paper can apply it to the synthesis of AgNWs over 60 microns or even 100 microns. Araki et al. [9] also further proved through their team's experiments that it is also a method to control the reaction temperature while changing the stirring speed. Its team has been able to manufacture super-long AgNWs with a length ranging from 20 to 100 microns. Some scholars Andrés et al. [12] have produced ultra-long silver nanowires with a length of $195\mu\text{m}$ under the above experimental conditions. Compared with traditional ITO, TCF based on AgNWs has a great advantage in performance characteristics. Although this paper has made enough progress, this paper only uses the above-mentioned polyols to prepare AgNWs, and the maximum length is about 200 microns, which is very limited. Therefore, the latest research goal is to discover an improved production method that can control the innovation of AgNWs in the length direction. This method is to add ascorbic acid to the traditional polyol in the synthesis process. This substance has an unexpected effect in promoting the growth of AgNWs. It can be found in the control group experiment that whether ascorbic acid is added or not has an amazing 2.7-times difference in length. Not only that, but the haze of AgNWs with amazing length produced by the improved method is only 1.35%. In this case, the optical transmittance of agnws is 92.61%, and $322 \Omega \text{ sq}^{-1}$.

2.3. Method for improving the conductivity of silver nanowire film

Because silver nanowires are one-dimensional nanomaterials, there are many choices for the arrangement of one-dimensional nanomaterials on the plane. Dr. Hu Hebing of Nanyang Technological University has rich experience arranging one-dimensional nanomaterials. He found that the conductivity of silver nanowires can be further improved by changing the arrangement mode of silver nanowires. The conventional characterization proves that the electrode's negative wires are vertically arranged network structures in the stretched state and entangled structures in the unstretched state. Moreover, this paper found that for single-layer silver nanowires, the conductivity in the alignment direction of silver wires is much higher than that in the vertical direction.

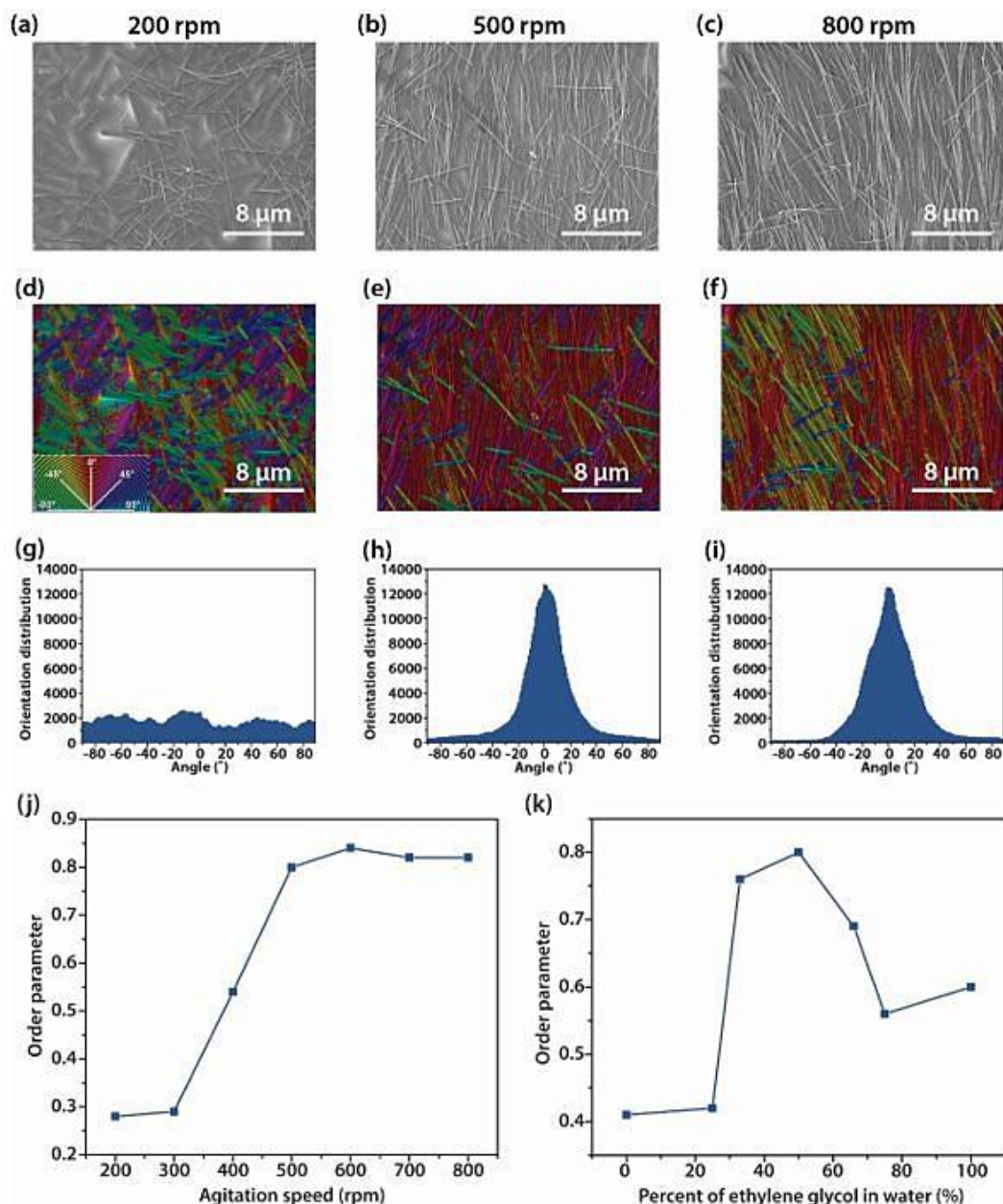


Figure 7. The SEM images, orientation-color-coded pictures and angular distribution of AgNWs thin films oriented at different speeds [11].

This paper also studied the factors affecting the arrangement of silver nanowires: stirring speed and solvent viscosity. Figure 7 shows that when the stirring speed is below 500 rpm, silver nanowires' alignment index increases with the It can be observed in fig. 7 that the stirring speed of silver nanowires will be a watershed at 500rpm, when the stirring speed is not higher than at 500rpm, the value of its arrangement direction will be obviously proportional to the stirring speed. On the contrary,

when the stirring speed exceeds 500rp, it will be found that this value has reached its peak value, and will not increase with the increase of stirring speed. However, in this case, the solution will be more active and there may be a risk of splashing. This work concludes that the stirring speed at 500rpm is the best required stirring speed, and the rotation data is the best at this time, so that the manufactured product will produce the best good conductivity. Fig. 7 (j- k) can help us draw a conclusion that the best orientation data can be obtained when the volume ratio of ethylene glycol to water is 1:1. The two situations are objective factors that will have great influence on the conductivity of conductive films.stirring speed. When the rate is more significant than 500 rpm, the alignment index is unchanged, but the solution will splash, so the best stirring speed is 500 rpm, and the alignment direction is more regular when rotating, which leads to better conductivity. From Figure 7 (j- k), the alignment index is the largest when the volume ratio of ethylene glycol to water is 1:1, and all these factors will greatly affect the conductivity of the transparent conductive film of silver nanowires.

3. Application of AgNW flexible transparent electrode

The performance of flexible transparent electrodes greatly impacts solar cells' photo-conversion efficiency. When employed in polymer solar cells, the AgNW electrode has shown to be a comparable alternative to conventional ITO electrodes [15]. Compared with traditional ITO materials, AgNW has higher optical transparency in the infrared range. Some applications of silver nanowires to construct flexible transparent electrodes and their applied characteristics are listed.

Table 1. Application of nanowires to construct the flexible transparent electrode

Application direction	Application Characteristics
Solar Cells	Low cost, Efficient
Lighting Devices	Good electroluminescent performance, Current density, Current efficiency, Driving voltage and brightness.
Touch Panels	High durability, Good touch panel performance, strong self-healing ability.
Flexible Sensors	Self-adjust sensor sensitivity
Transparent Heaters	High thermal conductivity, Can be heated quickly and uniformly in a large area (under specified conditions.)

Researchers have completed the production of the electrode made of AgNWs on a considerable scale, and will put it into practice in producing batteries with flexible and optically transparent solar electrodes. This research will explore the plasma effect to control the photoelectric effect [9]. The available function of the electrode made by plasma technology on its surface can be numerically controlled by a series of methods such as partial oxidation [11]. This work solved the problem of AgNWs surface by optimizing that the buffer zone of the non-thin active layer and non-thick layer is compressed and optimized. This method can also be used as a connector to reduce AgNWs grid roughness [8].

3.1. Space considerations Flexible sensor

At present, flexible sensors have been widely used, for example, in the field of human health monitoring, so that people can have a clearer understanding of their body function data, [12]. According to the report, researchers will make a connection and combination with the network formed by AgNW in the fields of strain, pressure and electrochemical sensors [3]. Designers will take into account factors such as linearity, detection range, sensitivity, response time, stretchability and stability when designing flexible and bendable conductors. But the main part is to explore its sensitivity and extensibility, the two parts that this papercare most. Considering that AgNW can

control the density of its nano-network on the two-dimensional plane of the surface to be different from its roughness, it can achieve a requirement of controllable sensitivity [20]. The two numbers of 50% and 90% are the lower limit and the upper limit of the stretching degree of the flexible foldable sensor under normal conditions [8]. Yao and Zhu can manufacture a new type of sensor with a pressure as high as 1.2 MPa⁹, which the instrument can detect. This strain sensor can still exert its excellent linearity when it is in a large strain of 50%. Due to the space, this paper will introduce the last two applications -Flexible sensor and Transparent heater in detail.

3.2. Line thickness Transparent heater

Because of the excellent thermal conductivity of the AgNW electrode, this paper can apply it to some functional electronic materials, such as the transparent heating instrument this paper will introduce next. At first, this application was made so drivers would not be bothered by frozen windows when driving cars and have been widely used for defrosting and defogging [13] [14] [15]. Recently, our interest has shifted to portable small-sized electronic devices. For example, it is applied to thawing goggles for heating a small amount of water. Figure 8. (a) is committed to finding a production mode with low cost and large production scale, and chose silver nanowire film with high flexibility to lower the working voltage limit and increase the temperature. With the development of electronic products with high flexibility, the transparent heater can work well under bending conditions, so people apply it to the flexible wrist. [Figure8, b] Under a suitable working voltage (about 12V), the transparent heater can be raised by more than ten degrees or even dozens of degrees. This device can quickly generate thermal response and uniform heating in a large area.

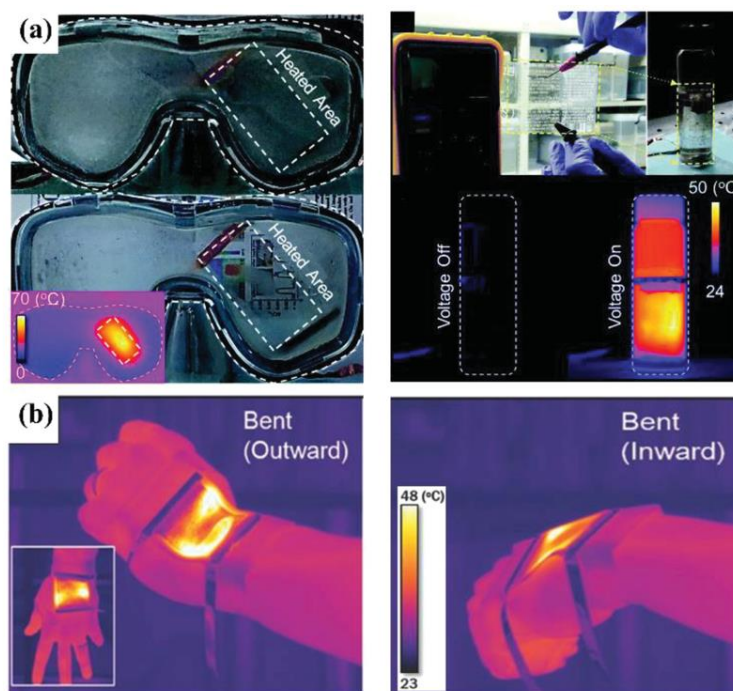


Figure 8. a) A flexible, foldable heating device with good optical transparency can be used to defrost goggles in cold outdoor or a bottle of water can be heated. b) A photo taken by a flexible transparent electrode heater that can be bent and folded under infrared conditions.

Figure 9 shows the transparent heater’s temperature response and heat tolerance under zero strain when the voltage values differ [Figure. 9.d] shows the reaction of different temperatures under different action conditions when the same voltage is given. The novel point is that due to the fast-switching characteristics caused by good thermal conductivity, the transparent heater based on AgNW can also be applied to temperature-related applications, such as thermochromic displays.

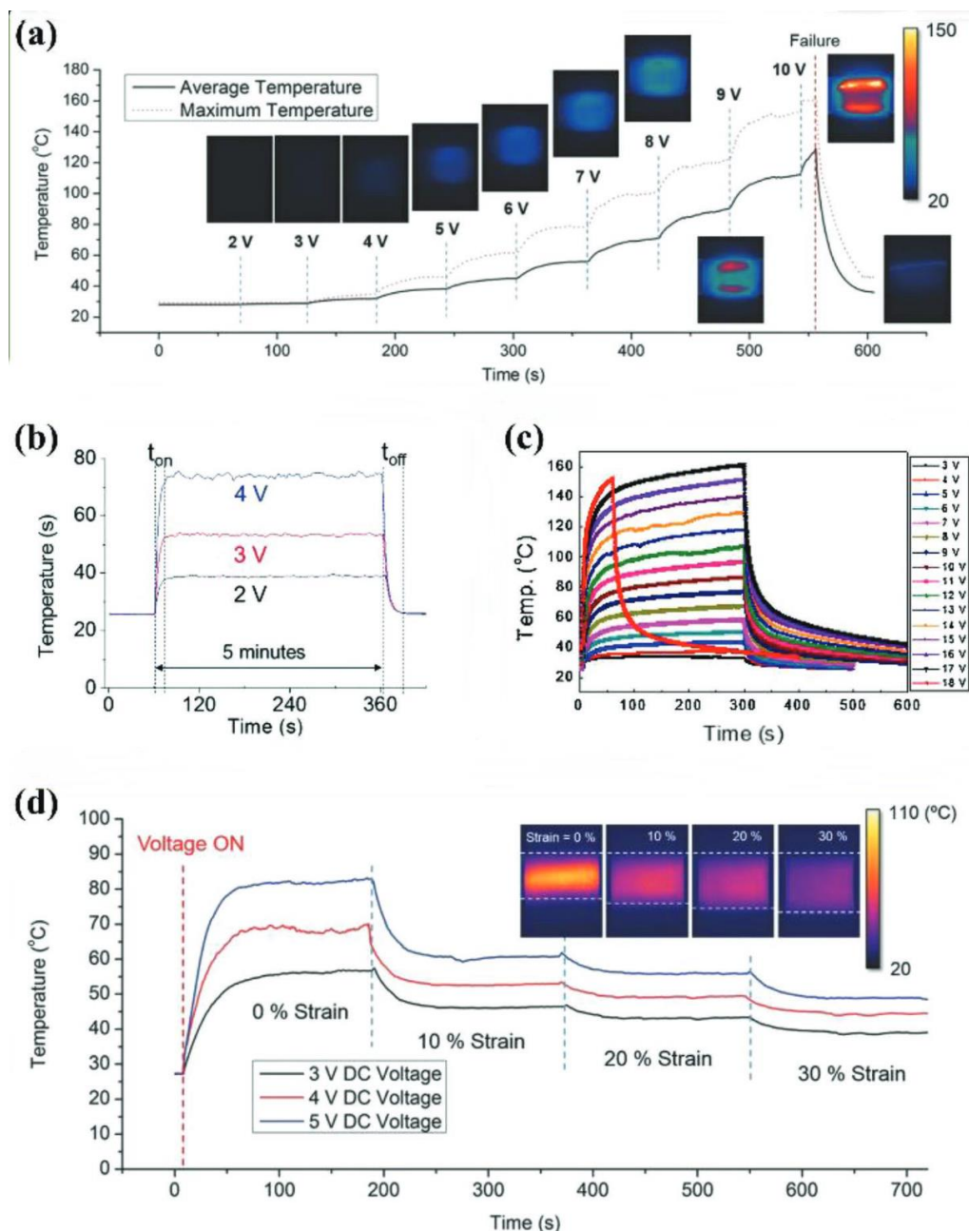


Figure 9. Schematic diagram of the flexible foldable transparent heater with temperature change: a) Instantaneous temperature change at zero strain under different voltage conditions. b) T The situation of different samples in the five-minute heat endurance test. c) The change of voltage under the condition of temperature. d) The transient temperature change process is in the same voltage condition.

4. Conclusion

This paper introduces us to the method of constructing flexible transparent electrodes by silver nanowires. Silver nanowires have excellent properties and the application of silver nanowires in constructing flexible transparent electrodes. According to this review, the AgNW network is a promising alternative to ITO, simple preparation process, and outstanding performance due to its excellent photoelectric and mechanical properties. This paper can develop a variety of electrodes based on AgNW, which have good optoelectronic properties and excellent mechanical flexibility. However, in practical use, AgNW as a flexible transparent electrode still has some shortcomings. [16]

This paper also explains the development and application of silver nanowire flexible transparent electrode for us according to the manufacturing method, performance introduction, performance improvement, future application, and prospects. Among them, it focuses on 1. The improvement measures and schemes of large-scale silver nanowire flexible transparent electrode production. To solve this problem, this paper introduces two preparation methods, Spin Coating and Meyer rod coating, to improve the yield and performance. 2. For the problems of high contact resistance, low stability, and low transmittance, which seriously hinder their application in the new generation of flexible wearable devices, this paper introduced the Meyer rod coating method and then sintered it under an infrared lamp. The material resistance would be greatly reduced from $80\Omega/\text{square}$ to $6\Omega/\text{square}$ at 300°C , and PVP would begin to decompose at 250°C . The transmittance of the thin film can reach 65%, which effectively solves the problems of high contact resistance, low stability, and low optical transmittance. 3 To solve the problem that silver nanowires exposed in the air are easily oxidized, this paper covers the flexible transparent electrode constructed by silver nanowires with Teflon to solve the problem that the electrode is easy to react with chemicals in the air, thus increasing the application environment of the manufactured electrode. Last but not least, focusing on the issue of lowering the surface roughness of AgNWs and managing the interface contact between AgNWs and the deposited layer in order to successfully lower the contact resistance, this article decided to apply GO to the surface of the manufactured AgNWS. The conductive film's surface roughness dramatically decreased when GO was covered. Additionally, the environment of the graphene-coated conductive AgNW sheet eliminates the interface contact between the deposited layer and the outside environment, increasing stability.

In this paper, although there are still some problems in the performance of flexible transparent electrodes constructed by AgNWs, with the emergence of generation after generation of flexible wearable optoelectronic devices, people's demand for the performance of flexible transparent electrodes has increased, and its prospects will be broader. The traditional electrodes constructed by ITO will eventually be developed at a rapid speed. AgNW networks are increasingly critical to the future development of electrochromic and polymer dispersive liquid crystal (PDLC) devices, transparent touch displays, electromagnetic protection and other technologies.

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