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Chapter 2

Fabrication and Applications of Flexible Transparent Electrodes Based on Silver Nanowires

Peiyun Yi, Yuwen Zhu and Yujun Deng

Additional information is available at the end of the chapter

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Abstract

There has been an explosion of interests in using flexible transparent electrodes for next-generation flexible electronics, such as touch panels, flexible lighting, flexible solar cells, and wearable sensors. Silver nanowires (AgNWs) are a promising material for flexible transparent electrodes due to high electrical conductivity, optical transparency and mechanical flexibility. Despite many efforts in this field, the optoelectronic performance of AgNW networks is still not sufficient to replace the present material, indium tin oxide (ITO), due to the high junction resistance. Also, the environmental stability and the mechanical properties need enhancement for future commercialization. Many studies have attempted to overcome such problems by tuning the AgNW synthesis and optimizing the film-forming process. In this chapter, we survey recent progresses of AgNWs in flexible electronics by describing both fabrication and applications of flexible transparent AgNW electrodes. The synthesis of AgNWs and the fabrication of AgNW electrodes will be demonstrated, and the performance enhanced by various methods to suit different applications will be also discussed. Finally, technical challenges and future trends are presented for the application of transparent electrodes in flexible electronics.

Keywords: flexible electronics, flexible transparent electrodes, silver nanowires, fabrication, application

1. Introduction

Flexible transparent electrodes are a crucial component in many devices, such as touch screen panels, solar cells, light emitting diodes (LEDs) and flexible sensors [1]. Although Indium tin oxide (ITO) is the dominant material with desirable performance for transparent electrodes currently, an alternative to ITO transparent electrodes has been widely studied in recent years...
due to the increasing marketing demand for flexible devices and the brittleness and scarcity of ITO.

Recent studies have suggested carbon nanotubes (CNT) [2, 3], graphene [4] and silver nanowires (AgNWs) [5] as the alternatives. Though CNTs are reported to have good electrical, thermal and mechanical properties, the CNT electrodes show lower electrical conductivity than ITO electrodes due to large contact resistance and extensive bundling of CNTs. Graphene is reported to have high Fermi velocity of 106 m/s and high intrinsic in-plane conductivity. But the large-area production of high-performance graphene films remains a serious issue. Although chemical vapor deposition method has the ability of producing large-area high-performance graphene, the process costs a lot and needs extremely high temperature.

Metallic nanowire based electrodes, as the most promising alternative to ITO, have superior optical, electrical and mechanical properties. Both random and regular metallic nanowire networks have received an increasing interest from both academia and industry. Random metallic nanowires can be dispersed in the solvent and be deposited onto the substrates through low-cost solution-based processing [6]. This makes nanowire-based electrodes compatible for high-throughput and large-area production of the next generation flexible optoelectronic devices. Moreover, for regular metallic nanowire based electrodes, called metal mesh, the electrical conductivity and the optical transparency can be easily tuned by changing the geometry parameter of the nanowires. When the period of the metal mesh is in sub-micrometer scale and the line width is close to subwavelength, metal meshes can be considered as bulk materials to estimate the sheet resistance of the films. Various metallic materials, such as gold, silver and copper, are used to achieve different work functions and chemical properties for various applications. Silver, a material with high electrical conductivity and low price to some degree, is considered as the most suitable nanowire material. And the overall performance of AgNW electrodes has already surpassed that of ITO electrodes. Table 1 shows the comparison of several transparent electrodes based on different materials.

The present chapter focuses on recent progresses in the fabrication techniques of flexible transparent AgNW electrodes. Firstly, we briefly introduce the requirements of electrical, optical, thermal and mechanical properties for flexible transparent electrodes in different applications. Then synthesis of AgNWs and film-forming techniques of flexible transparent AgNW

<table>
<thead>
<tr>
<th>Properties</th>
<th>ITO</th>
<th>TCO</th>
<th>CNT</th>
<th>Graphene</th>
<th>AgNW</th>
<th>Ag mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Transmittance</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Haziness</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Flexibility</td>
<td>--</td>
<td>--</td>
<td>+++</td>
<td>+++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Stability</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Large-scale</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>++</td>
<td>--</td>
</tr>
<tr>
<td>Low-cost</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 1. Comparison of several transparent electrodes.
electrodes will be introduced. Thirdly, recent investigations in optimizing all the properties of flexible transparent electrodes will be discussed in detail. Finally, the future challenges in the widespread adoption of flexible transparent AgNW electrodes will be proposed.

2. Requirements for flexible transparent electrodes in different applications

Flexible transparent electrodes can be applied in many cases. Different properties are required according to different applications subject to various problems, as shown in Table 2. In this section, we will introduce some applications such as touch panels, solar cells, flexible lighting, and flexible sensors.

2.1. Touch panels

Touch Display Research Inc. forecasted that the market of transparent electrodes without ITO will reach $13 billion by 2023. The surface area of manufactured touch panels will reach more than 80 km$^2$ in 2025, double of that in 2014, predicted by IDTechEx Ltd. [7]. Companies like Samsung, LG, Apple and Toshiba have all indicated the market trends for flexible displays. Touch screens can be divided into capacitive sensing and resistive sensing by different working principles. When fingers touch the screen, the capacitive sensing works on the change in capacitance instead of the change in resistance as the resistive sensing does. Resistive sensing is low-cost and high-resolution reported by S.H. Ko's team [8, 9]. With the durability and the compatibility of multi-touch features, the capacitive sensing arises many researchers’ attention worldwide. Capacitive touch panels can now be divided into single [10–12] and double-sided sensors [13, 14] based on the number of transparent conductive layers. Figure 1(a) and (b) show the photograph of the working touch panel [10]. The resolution of single-sensor capacitive touch screen is required to be at the millimeter scale while that of double-sided ones is hundreds of micrometers. Not only the distribution but also the orientation and alignment will govern the performance of the AgNW networks. Patterning is also of prime importance for high performance. Figure 1(c) exhibits the design of touch sensors and the image

<table>
<thead>
<tr>
<th>Properties</th>
<th>ITO</th>
<th>TCO</th>
<th>CNT</th>
<th>Graphene</th>
<th>AgNW</th>
<th>Ag mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>---</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Transmittance</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Haziness</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Flexibility</td>
<td>---</td>
<td>---</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>-</td>
</tr>
<tr>
<td>Stability</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Large-scale</td>
<td>-</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Low-cost</td>
<td>---</td>
<td>-</td>
<td>-</td>
<td>---</td>
<td>+++</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 2. Comparison of performance requirements for different applications.
of patterned AgNW networks respectively [12]. Interestingly, healable touchscreens were produced by Pei and co-workers through embedding AgNWs into the surface of healable polymer substrate [14], as shown in Figure 1(d).

2.2. Solar cells

Flexible transparent electrodes as front electrodes is a crucial factor in determining photovoltaic performance of solar cells [15]. High electrical conductivity and high optical transparency of flexible transparent electrodes are required in order to lower the ohmic dissipation of heat and maximize the light absorption in the conversion layer. The band alignment and work function of the electrodes should also be considered. The most commonly used materials for solar cells are doped metal oxides. They are prone to cracking, costly and need high-temperature fabrication. Many researches have proved that AgNW networks are a promising alternative to ITO for both organic solar cells [16–18] and polymer solar cells [19]. AgNW networks have similar photovoltaic performances and excellent bending capacities as ITO and are compatible with solution-processed fabrication. And unlike doped metal oxides, AgNWs have high optical transparency in the IR range, leading to enhanced efficiency and the semi-transparency of solar cells. The performance comparison in solar cells using AgNW electrodes

<table>
<thead>
<tr>
<th>PCE(%)</th>
<th>Jsc(mA/cm²)</th>
<th>Voc(V)</th>
<th>FF(%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.85</td>
<td>-7.22</td>
<td>0.5308</td>
<td>48.475</td>
<td>[20]</td>
</tr>
<tr>
<td>6.58</td>
<td>14.29</td>
<td>0.78</td>
<td>59</td>
<td>[1]</td>
</tr>
<tr>
<td>3.05</td>
<td>9.191</td>
<td>0.638</td>
<td>0.521</td>
<td>[21]</td>
</tr>
<tr>
<td>2.73</td>
<td>8.4</td>
<td>0.58</td>
<td>56.07</td>
<td>[22]</td>
</tr>
<tr>
<td>2.66</td>
<td>6.36</td>
<td>1.06</td>
<td>39.59</td>
<td>[19]</td>
</tr>
</tbody>
</table>


Table 3. Performance comparison in solar cells.
is shown in Table 3. Topics concerning the integration of transparent AgNW electrodes into flexible solar cells are as follows: one is the low-cost fabrication for the development of flexible solar cells and another one is the study of plasmonic effects to further control the optoelectronic properties.

2.3. Flexible lighting

AgNW electrodes can be integrated into LEDs. Figure 2(a) shows the schematic of AlGaN-based LEDs with AgNW/ITO electrodes [23]. The active layer of the light emitting devices mostly investigated can be organic materials (OLEDs) or polymer (PLEDs). The emulation of fully rollable lighting panels is time-to-market dependent on our ability to provide not only the active layer but also the interfaces and the transparent electrodes with high flexibility. In this case, it is essential for the transparent electrodes to have no alteration in optoelectronic properties under bending cycles. For conventional ITO-based OLEDs, the luminance and the efficiency of the devices would have a sharp decrease under mechanical stress due to the fracture of the brittle ITO electrodes. Thus the usage of AgNW electrodes with good optoelectronic and mechanical properties seems to be a good strategy to fulfill this demand. Polyvinyl alcohol (PVA) [24], polyacrylate [25], poly(methyl methacrylate) (PMMA) [26], colorless polyimide (cPI) [27] and poly(urethane acrylate) (PUA) [28, 29] are used to produce the transparent electrodes together with AgNWs to improve the performance of electrodes. For instance, AgNW/PMMA OLEDs show high luminous efficiency, the color-independent emission and the nearly perfect Lambertian emission [26], as depicted in Figure 2(b). Many efforts have been done to decrease the current leakage [30, 31]. Table 4 illustrates the performance comparison of LEDs produced by different researchers. The challenge of keeping the performance of AgNW-based OLEDs unchanged under deformation also arises many researchers’ attention [28].

2.4. Flexible sensors

High sensitive and stretchable sensors can be used in both our daily life and large military projects, from the human health monitoring devices to the structural health monitoring of aircrafts and bridges [36–38]. Figure 3(a) shows a strain sensor attached to the neck to monitor human activities [39]. And as shown in Figure 3(b), AgNW electrodes can be integrated
into electrocardiogram (ECG) measurements [38]. Performances of flexible sensors concern about the linearity, sensitivity, detecting range, response time, stability and stretchability. Investigations using AgNW electrodes mainly concern about strain sensors [40, 41], pressure sensors [40] and electrochemical sensors [42]. Yao et al. presented wearable sensors based on highly stretchable AgNW electrodes enabling the detection of strain and pressure [40]. The strain sensors produced showed good linearity and reversibility even up to a large strain of 50%. At the same time, the pressure under detection ranged up to 1.2 MPa. Hwang et al. have recently developed a self-powered patchable platform to monitor human activities [39], as shown in Figure 3(c). Usually, the stretchability of the transparent systems has been reported to be among 50–90% [43, 44]. The high stretchability is achieved by compositing AgNWs with a thin layer of elastomer [39, 41]. In particular, Jeong et al. integrated ultra-long AgNWs into an elastic-composite generator which exhibits hyper-stretchability up to 200% [45], as shown

<table>
<thead>
<tr>
<th>Category</th>
<th>Vc(V)</th>
<th>EQE(%)</th>
<th>CE(cd/A)</th>
<th>PE(lm/W)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLED</td>
<td>NA</td>
<td>NA</td>
<td>58.2</td>
<td>NA</td>
<td>[32]</td>
</tr>
<tr>
<td>OLED</td>
<td>NA</td>
<td>18.7</td>
<td>68.6</td>
<td>62.8</td>
<td>[33]</td>
</tr>
<tr>
<td>OLED</td>
<td>6</td>
<td>24.3</td>
<td>49</td>
<td>30.3</td>
<td>[26]</td>
</tr>
<tr>
<td>PLED</td>
<td>0.6</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>[34]</td>
</tr>
<tr>
<td>LED</td>
<td>2.72</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>[35]</td>
</tr>
<tr>
<td>OLED</td>
<td>3.6</td>
<td>NA</td>
<td>44.5</td>
<td>35.8</td>
<td>[30]</td>
</tr>
</tbody>
</table>

Table 4. Performance comparison in LEDs.

Figure 3. The schematic and photograph of flexible AgNW sensors: (a) photograph of strain sensor attached to the neck [39], (b) AgNW dry electrode for ECG measurements [38], (c) the schematic diagram of strain sensor [39], and (d) the schematic illustration of highly-stretchable nanocomposite generator [45].
in Figure 3(d). In addition to stretchability, the sensitivity can be tuned by controlling the areal density and roughness of AgNW networks [46]. Further optimization of geometry and materials is needed in this field.

3. Fabrication of flexible transparent electrodes based on silver nanowires

3.1. Controllable synthesis of silver nanowires

Many approaches have been addressed to synthesize AgNWs, which can be mainly divided into two groups: template methods and polyol process [47]. Template methods are classified into two categories, in terms of hard templates and soft templates. Soft templates include polymer film of PVA and DNA chains [48, 49]. Hard templates include silicon wafer and aluminum oxide [50, 51]. Although many literatures have investigated template methods to synthesize AgNWs, these methods are incompatible for large-scale production. The preparation and removal of the templates are time consuming and high cost. Moreover, nanowires synthesized through template methods suffer from low aspect ratio, irregular morphology and low yield.

Different from template methods, polyol process provides high yield of nanowires with ideal morphology. As the most promising synthetic procedure, salt-mediated polyol method [52, 53] has good reproducibility and low cost. The usage of salts, such as NaCl [54], CuCl₂ [53], CuCl [53], FeCl₃, and PtCl₂, helps the mass synthesis of AgNWs. Metal seeds in the solution served as nuclei for subsequent growth of AgNWs, as depicted in Figure 4(a). The dimensions of AgNWs can be kinetically controlled by temperature, seeding conditions, and the ratio between PVP and AgNO₃. High reaction temperature leads to the formation of nanowires with low aspect ratio. Increasing the concentration of metal seeds could slightly decrease the diameter of nanowires. Chen et al. [55] adjust the concentration of Na₂S to control the diameter of AgNWs. The aspect ratio of the nanowires is small, unable to meet the requirements for high aspect ratio nanowires. Microwave and UV irradiation have been adopted by researchers to assist the synthesis of AgNWs [56–58]. The controllable methods to fabricate high aspect ratio nanowires have received much attention. Long nanowires with length of over 300 μm were fabricated by Lee et al. [59] using a successive multistep growth method, as shown in Figure 4(b). The fabrication process is time-consuming and complex. Then Andrés et al. [60] demonstrated a rapid synthesis of nanowires with the length reaching 190 μm to overcome this problem.

3.2. Coating techniques

Apart from the synthesis of AgNWs, coating and printing them onto the flexible plastic substrate is also an essential process in the fabrication of transparent electrodes. The performance of the electrodes varies according to different techniques and devices. The ideal process should meet three requirements: (1) the process should be free from toxic chemicals and costly materials; (2) the process should have a low environmental impact and can be recycled; (3) the process should meet the demand of the large-area, high-efficiency and high-quality production. Solution-processed fabrication can easily be surface scalable. Many solution processes have been reported to produce
AgNW electrodes, including Meyer rod coating [5, 33, 62, 63], dip coating [64], spin coating [65–67], drop casting [68], spray coating [69], vacuum filtration [70], roll-to-roll printing [19, 71, 72] and transferring [73, 74]. Figure 5(a)-(e) show coating devices with different techniques. Most of the
techniques are compatible with low-energy deposition process and without any vacuum equipment. Direct laser ablation [13, 75], shadow mask [11], chemical etching using the photolithography process [76] are all the patterning strategies for flexible transparent electrodes.

3.2.1. Roll-to-roll techniques

The processability of AgNW networks by R2R was showed by many researchers due to their compatibility with large-area production [81–83]. The substrate in R2R coating system is required to have mechanical flexibility and in the form of a long sheet. Quite different from other solution-processed coating methods, the R2R process is continuous and is suitable for large-area production. During coating, the substrate is first unwound from a roll and then passed through the coating machine and finally rewound on another roll. Aside from the coating machine, some post-treatment may also be added into the process, such as compressing, heating, UV-curing, chemical welding and drying, as shown in Figure 6(a) [83]. Interestingly, Lai’s team produced AgNW electrodes combined with moth-eye nanostructures using R2R techniques and greatly enhanced the transmittance [5, 81]. The quality of forming can be influenced by tension, speed, cleaning of the substrate and the removal of static electricity. Also, the pre-treatment and post-treatment can have a great impact on the performance of the coated AgNW films. Many laboratories have developed their own R2R system to study the coating process. Figure 6(b)-(d) show two laboratory-scale coating system [77, 84]. Hösel et al. have compared the performance of flexible electronics produced by R2R process [85]. The biggest challenge of R2R process is the unification problem [86]. The comparison between different printing methods for large-scale R2R production was reported in Roll-to-Roll Processing Technology Assessment by U.S. Department of Energy, as shown in Table 5 [87].

Figure 6. The schematic and equipment of roll-to-roll fabrication process: (a) the schematic [82], (b) photograph of the R2R system [84], (c) a laboratory-scale coating system from solar coating machinery GmbH, Germany [77], and (d) photograph of the monitoring during coating [77].
3.2.2. Drop casting

Drop casting is the simplest method to produce flexible transparent electrodes. The equipment needed is only a horizontal work platform. What we need to do is casting the coating solution onto the substrate followed by drying. However, problems exist due to the simple procedure. The thickness of the film is unable to be controlled. The effect of “coffee-ring” may be easily observed causing uneven distribution of nanowires due to the surface tension of the liquid and the self-aggregation of nanowires upon drying.

3.2.3. Spin coating

Spin coating is an important way to form homogeneous film. As illustrated in Figure 7(a), the substrate is first accelerated to a chosen rotational speed and then the coating solution is applied onto the substrate followed by drying. However, problems exist due to the simple procedure. The thickness of the film is unable to be controlled. The effect of “coffee-ring” may be easily observed causing uneven distribution of nanowires due to the surface tension of the liquid and the self-aggregation of nanowires upon drying.

3.2.4. Screen printing

Screen printing has a large wet film thickness. The coating ink used needs to have a high viscosity and low volatility. First, the screen should be under tension by being glued to a frame. Second, an emulsion is filled into the screen to obtain the pattern. Here the area of the emulsion should be with no print and the area of the pattern is open waiting for the coating ink.

<table>
<thead>
<tr>
<th>Printing method</th>
<th>Speed</th>
<th>Wet thickness (μm)</th>
<th>Resolution (μm)</th>
<th>Start/Stop</th>
<th>Complexity</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flatbed Screen Printing</td>
<td>Low</td>
<td>5–100 μm</td>
<td>100 μm</td>
<td>Yes</td>
<td>Low</td>
<td>Limited</td>
</tr>
<tr>
<td>Rotary Screen Printing</td>
<td>High</td>
<td>3–500 μm</td>
<td>100 μm</td>
<td>Yes(α)</td>
<td>Medium</td>
<td>Very good</td>
</tr>
<tr>
<td>Inkjet Printing</td>
<td>Medium</td>
<td>1–5 μm</td>
<td>&lt; 50 μm</td>
<td>Yes</td>
<td>High</td>
<td>Limited, materials must be jettable</td>
</tr>
<tr>
<td>Flexography</td>
<td>Very high</td>
<td>1–10 μm</td>
<td>&lt; 50 μm</td>
<td>Yes(α)</td>
<td>Medium</td>
<td>Very good</td>
</tr>
<tr>
<td>Imprint or soft lithography</td>
<td>High (&gt; 5m/min)</td>
<td>NA</td>
<td>0.1 μm</td>
<td>NA</td>
<td>NA</td>
<td>New technology</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Low</td>
<td>NA</td>
<td>~10 μm</td>
<td>NA</td>
<td>NA</td>
<td>Thermal effect sensitivity</td>
</tr>
<tr>
<td>Gravure</td>
<td>High</td>
<td>NA</td>
<td>&gt; 0.07 μm</td>
<td>NA</td>
<td>NA</td>
<td>Very good</td>
</tr>
</tbody>
</table>

(a)-Stopping should be avoided. Risk of registration lost and drying of ink in anilox cylinder. Short run-in length. NA-not available.

Table 5. Comparison between different printing methods in terms of their theoretical capacity and practical applicability for large-scale R2R production [87].
Third, the patterned electrodes is obtained by filling the screen with coating ink. Figure 8(a)-(c) show screen printers both in laboratories and factories, while Figure 8(d) shows the screen printing process.

4. Performance enhancements of flexible transparent electrodes

4.1. Optoelectronic properties

The optimization of the optoelectronic properties has been studied for many years. Since junction resistance plays an important role in the electrical properties of the whole network, decreasing
the number of junctions and reducing the junction resistance between wires are two main ideas to lower the sheet resistance of the film. In order to decrease the number of junctions, some researchers have studied different approaches to synthesize nanowires with high aspect ratio [59, 60, 89], which have been introduced in Section 3.1. Researchers have also devoted great efforts to decrease the junction resistance between nanowires. Methods such as vacuum filtration [90], graphene coating [91, 92], electrochemical coating [93], modification with graphene oxide (GO) [29] and deposition of particles like Au, ZnO and TiO$_2$ [94] have been performed in the fabrication of transparent electrodes to reduce the resistance. Liang et al. wrapped the GO sheet around AgNW junctions and obtain a flexible transparent electrodes with the sheet resistance of 14 Ω/sq. and the transmittance of 88%, as shown in Figure 9(a) [29]. Many post-treatments such as thermal annealing [24], pressing [95], electrochemical annealing [96], salt treatment [83, 90], plasmonic welding [97], HCl vapor treatment, capillary-force-induced cold welding [63] and high intensity pulsed light technique (HIPL) [98, 99] have also been studied to reduce the junction resistance. Figure 9(b) and (c) show the obvious changes of AgNW junctions after hot-pressing. Lee et al. [6] demonstrated that annealing of the nanowire network at the temperature of 200°C causes the PVP to flow and partially decompose, leading AgNWs to fuse together. However, thermal annealing needs high temperature and long treatment time. It also cannot be employed with heat-sensitive substrates. Tokuno et al. [100] performed two steps to replace the heat treatment in the fabrication of transparent electrodes. The network was first rinsed with water and ethanol to remove the PVP followed by mechanical pressing to weld the wires. The sheet resistance was

Figure 9. Different methods to improve the optoelectronic properties of flexible transparent AgNW electrodes: (a) SEM observation of AgNW networks with GO surrounding AgNW junctions [29]. (b-c) SEM images of AgNW networks before and after hot-pressing [32]. (d) a schematic diagram of electrowelding treatment [101]. (e) illustration of the procedure used for the preparation of dual-scale nanowire networks [33]. and (f) SEM image of AgNWs bridging graphene grains [104].
reduced from $6.9 \times 10^6$ to $1.8 \times 10^4 \, \Omega/$sq. and then to $8.6 \, \Omega/$sq. However, mechanical pressing may not suitable for delicate substrates. Thus some other different approaches such as joule heating, HIPL, moisture-treating and hybridization with mesoscale wires, have been explored. Song et al. [101] apply the idea that joule heating can weld platinum wires and carbon nanotubes into the metallic nanowire networks. An approach with low additional power and short treatment durations is achieved by current-assisted localized joule heating accompanied by electromigration, as shown in Figure 9(d). The resistance of individual nanowires is also investigated by researchers, such as the utilization of nanowires with large gain size [102] and the hybridization of different scale wires [33, 103]. Figure 9(e) shows the procedure used to produce dual-scale nanowire networks [33]. Many investigations also focus on hybridizing AgNWs with other conductive materials. AgNWs were treated as bridges for high resistance grain boundaries of graphene by Teymouri et al. to obtain highly transparent electrodes, as shown in Figure 9(f) [104].

Besides the electrical properties, many efforts have been done by researchers to improve the optical transparency of AgNW electrodes. Firstly, the dimensions of AgNWs are optimized for high transmittance. Nanowires networks with large aspect ratio show better optical property [105]. Secondly, different deposition process has been explored. Kim et al. [79] applied the electrostatic spray deposition to obtain electrodes with the transmittance of 92.1%. Thirdly, changing substrates into more transparent materials. Jiang et al. [106] changing the commonly used polyethylene terephthalate (PET) substrate into the flexible resin film and improve the transmittance by nearly 10%. Kim et al. integrated CNT into AgNW electrodes to reduce the haze factor by absorbing the scattered light from AgNWs [107]. Table 6 illustrates the performance comparison in AgNW electrodes.

### 4.2. Environmental stability

Though environmental stability seems to be important for future application, few investigations have been reported so far on it compared to the optoelectronic performance. The

<table>
<thead>
<tr>
<th>NW dimensions</th>
<th>Substrate</th>
<th>Rs ((\Omega/$sq)</th>
<th>T (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D 20–40 nm, L 20–40 (\mu m)</td>
<td>Glass/PET</td>
<td>91.3</td>
<td>97.9</td>
<td>[108]</td>
</tr>
<tr>
<td>D 35 nm, L 25 (\mu m)</td>
<td>PET</td>
<td>~50</td>
<td>94.5</td>
<td>[1]</td>
</tr>
<tr>
<td>D 25 nm, L 35 (\mu m)</td>
<td>PET</td>
<td>~20</td>
<td>86</td>
<td>[5]</td>
</tr>
<tr>
<td>D 20–90 nm, L 20–150 (\mu m)</td>
<td>PDMS</td>
<td>179</td>
<td>89.4</td>
<td>[63]</td>
</tr>
<tr>
<td>D 100 nm, L 100 (\mu m) and D 40 nm, L 10 (\mu m)</td>
<td>Resin</td>
<td>50</td>
<td>90</td>
<td>[33]</td>
</tr>
<tr>
<td>D 50–90 nm, L 15–25 (\mu m)</td>
<td>PEN</td>
<td>12</td>
<td>83</td>
<td>[32]</td>
</tr>
<tr>
<td>D 70 nm, L 8 (\mu m)</td>
<td>glass</td>
<td>6–21</td>
<td>70–85</td>
<td>[21]</td>
</tr>
<tr>
<td>D 70 nm, L 10–20 (\mu m) and D 85 nm, L 30–60 (\mu m)</td>
<td>PU</td>
<td>6</td>
<td>68</td>
<td>[98]</td>
</tr>
<tr>
<td>D 70 nm, L 200 (\mu m)</td>
<td>No data</td>
<td>&lt;30</td>
<td>95</td>
<td>[104]</td>
</tr>
<tr>
<td>Not available</td>
<td>Glass</td>
<td>11</td>
<td>87</td>
<td>[34]</td>
</tr>
<tr>
<td>D 115 nm, L 20–50 (\mu m)</td>
<td>PET/PEN</td>
<td>5</td>
<td>92</td>
<td>[83]</td>
</tr>
</tbody>
</table>

**Table 6.** Performance comparison in AgNW electrodes.
thermal conductivity of AgNWs and their degradation mechanism is lack of investigations. Mayousse et al. spend over 2 years to study the relationship between the stability of AgNW networks and the temperature, humidity, light, hydrogen sulfide and electrical stress [11]. Khaligh et al. [109] once modeled the random AgNW networks in MATLAB and analyzed the overall circuit with HSPICE. In their work, graphene can slow the degradation of AgNWs and uniform the surface temperature. In this case, the failure mechanism is not the nanowire degradation any more. It is changed into the melting of the substrate. Thus the most commonly used method is to use hybrid materials to improve both thermal and chemical stability. Also, the aging of flexible transparent electrodes under different working conditions is now lack of research. Song et al. compared the environmental stability of nanowires with nanoparticle coating and sol–gel TiO$_2$ coating [110]. As shown in Figure 10(a), AgNWs can easily react with sulfur ions to form Ag$_2$S (dark gray). Nanoparticles can reduce the exposure area but are unable to diminish the whole area. AgNWs with nanoparticles coating can still react with sulfur ions. The sol–gel TiO$_2$ avoid AgNWs being exposed to sulfur ions and improve the chemical durability of AgNWs.

4.3. Mechanical properties

The sheet resistance of transparent AgNW electrodes shows negligible increase under bending test, quite different from that of ITO electrodes. AgNWs are able to conform to non-planar surface. They can easily fit to the surface, even the highly roughened surface. Though the flexibility makes AgNW a promising alternative to ITO, the high roughness of the network remains a serious problem which hinders the development of AgNW electrodes. The high roughness would lead to interlayer shorting, high leakage currents, and low quantum efficiency in OLEDs [33]. The buffer layer and the conductive material coating are investigated by many researchers to reduce the roughness of the networks [111–114]. Nevertheless, they would degrade the performance by increasing the driving voltage and the electron–hole imbalance [30]. Burying AgNW into polymer substrate is also a way to reduce the roughness, but the effective electrode areas decreased [33]. In order to overcome this problem, the plasma treatment was applied on AgNW-cPI composite electrodes to enlarge the conductive
pathways, as shown in Figure 10(b) [27]. Intense-pulsed-light irradiation and the UV-Ozone treatment are also ways to smooth the film without any severe deterioration in the optical performance [22, 115].

The poor adhesion to substrates, together with the roughness and reduced effective electrical area, hinders the widely application of AgNW electrodes. Strong bonding is essential to avoid detachment of AgNW networks and maintain electrical conductivity at high strain deformation. Modifying substrate surface [74, 116], applying strong conformal pressure, in situ polymerization [24, 25, 94] and surface encapsulation [71] can effectively improve the adhesion. These methods are complex and time consuming, together with changing the properties of the substrates. In recent papers, some new methods have also been put forward. It is a fast and simple method compared with conventional approaches embedding nanowires into polymers [98]. Khan et al. [117] proposed a facile method to make the nanowires a nail-like structure which can be fully embedded in plastic films, greatly enhancing the wire-substrate adhesion.

5. Conclusion

The aim of this chapter is to demonstrate the fabrication techniques of flexible transparent AgNW electrodes and the efforts made to enhance the performance. Though AgNW electrodes reported exhibit similar performances to ITO electrodes, there is still a long way to go for future commercialization. Firstly, new synthesis methods for fine-tuning the dimensions of AgNWs are needed. The performances of AgNW electrodes have a close relationship with the dimensions of AgNWs. Secondly, metals other than silver need investigations to reduce the cost of electrodes with similar performances, such as copper. Thirdly, the hybrid materials, such as core-shell Cu-Ni nanowires and sandwich structure, are also of interest. Fourthly, the stability optimization in real environments is lacking now. The evaluation of the intrinsic stability is an important value to prove the possibility of integrating nanowires into future devices. Finally, the toxicity of nanowires needs attention before being integrated into commercial devices.

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Conflict of interest

There are no conflicts of interest.
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