Syntheses of Silver Nanowires Ink and Printable Flexible Transparent Conductive Film: A Review

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Abstract: Nowadays, flexible transparent conductive film (FTCF) is one of the important components of many flexible electronic devices. Due to comprehensive performances on optoelectronics, FTCF based on silver nanowires (AgNWs) networks have received great attention and are expected to be a new generation of transparent conductive film materials. Due to its simple process, printed electronic technology is now an important technology for the rapid production of low-cost and high-quality flexible electronic devices. AgNWs-based FTCF fabricated by using printed electronic technology is considered to be the most promising process. Here, the preparation and performance of AgNW ink are introduced. The current printing technologies are described, including gravure printing, screen printing and inkjet printing. In addition, the latest methods to improve the conductivity, adhesion, and stability of AgNWs-based FTCF are introduced. Finally, the applications of AgNWs-based FTCF in solar cells, transparent film heaters, optoelectronic devices, touch panel, and sensors are introduced in detail. Therefore, combining various printing technologies with AgNWs ink may provide more opportunities for the development of flexible electronic devices in the future.

Keywords: silver nanowires; conductive ink; printed electronic technology; flexible transparent conductive film

1. Introduction

With the development of science and technology, the application of flexible devices is gradually expanding. Compared with previous rigid devices, flexible devices gradually obtain some replacement of them due to the advantages of being stretchable, having high longevity, and available work efficiency. Flexible transparent conductive film (FTCF) has played an important role in flexible devices in recent years. As we all know, indium tin oxide (ITO), with its considerable transmissivity, was a popular material in the last two decades. However, the deficient properties of toxicity, brittleness, and expensiveness have limited ITO applications in flexible devices. Therefore, researchers now dedicate themselves to seeking candidates for FTCF, including silver nanowires (AgNWs), mental meshes, carbon nanotubes, and reduced oxide graphene (rGO). AgNWs as an emerging alternative to ITO, on account of good electrical conductivity, remarkable optical transparency, excellent mechanical flexibility, and compatibility, are the functional materials of many flexible devices, as shown in Figure 1a, such as solar cells [1,2], touch panels [3], organic light-emitting diodes (OLEDs) [4], polymer light-emitting diodes (PLEDs) [5], sensors [6,7], photodetectors [8,9], electrochromic devices [10], flexible thin film transistors (TFTs) [11], electromagnetic interference (EMI) shielding materials [12], and supercapacitors [13]. AgNWs is a one-dimensional linear material with a high aspect ratio (ratio of length to diameter, AR) which is closely in connection with its synthesis method. In addition to
the above-mentioned flexible devices, AgNWs has even been applied to biological fields [14–16] such as artificial synapse [14], dye degradation [15], and water splitting bifunctional electrocatalysts [16]. Herein, among the existing research achievements, it has been the perpetual goal to continue to improve the conductivity, transmittance, and stability of FTCF [17].

Figure 1b displays requirements of the essential performances of FTCF. The foremost two properties of FTCF are electrical and optical performances. Normally, the basic requirements of most flexible devices are that the transmittance is higher than 70% and the sheet resistance is lower than 100 Ω/sq [18]. However, the requirements of precise devices are often higher than these. In addition, chemical stability, thermal stability, and corrosion resistance of FTCF are also required. In terms of mechanical properties, it is usually required to keep the sheet resistance unchanged after multiple bending.

In recent decades, printable materials have become a promising research field. Furthermore, with the development of various electronic devices, micro-electronic printers have gradually occupied a place which provides the equipment foundation for fabricating FTCF by printing. The printing technology offers simplification with regard to the traditional preparation technology of flexible devices and, to some extent, makes plentiful improvements in terms of efficiency [15–20]. Figure 2 displays the modes of interaction between light and AgNWs-based FTCF, including reflection, transmittance, and scatter with light incident on the AgNWs-based FTCF. Generally, with the decreasing density of AgNWs, the transmissivity increases and the sheet resistance ($R_s$) decreases, respectively. How to lessen $R_s$ without losing transmissivity is therefore a tough prospect because they are contradictory.

Figure 1. (a) Applications of AgNWs-based flexible transparent conductive film (FTCF). Reprinted with permission from [19]; Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Requirements of essential performance of FTCF [20].

Figure 2. Interaction between light and AgNWs-based FTCF.
With the development of flexible electronic devices, printed electronics technology has gradually been investigated [8–15]. However, there are few reviews related to the printing of AgNWs inks. There is an overview of printed devices, but the technical points of printing AgNWs inks are not summarized in detail [21–24]. Herein, we introduced the preparation methods and key properties of AgNWs ink, and summarized gravure printing, screen printing, inkjet printing, and further compared the characteristics between them. In addition, we introduced five main applications of AgNWs-based FTCF and analyzed their performance requirements.

2. AgNWs Conductive Ink

Until now, many synthesis methods of AgNWs have been developed, which can be roughly divided into four categories: template method [25], electrochemical [26], wet chemical method [27], and poly method [28]. However, it is still a difficult problem to prepare large-scale AgNWs with controllable morphologies. This is also a bottleneck of restricting AgNWs-based FTCF further development.

Conductive ink is the pivotal material to realize printing technology. It can be said that the performance of conductive ink directly determines the quality of FTCF [29–35]. The components of conductive ink mainly include conductive fillers, solvent, adhesive phase, and functional additives. The functional additives include surfactant, dispersion stabilizer, moisturizer, pH regulator, defoamer, leveling agent, etc. Until now, silver nanostructure conductive inks used to make transparent conductive films are mainly silver nanoparticles (AgNPs) [29–31] or AgNWs [35–37], some of which have been compounded with highly conductive graphene [32] or polymer [33]. As the conductive filler of ink, the mass content of AgNWs is related to the conductivity of printed FTCF. Generally, the mass content of AgNWs determines the conductivity of FTCF. The solvent of AgNWs conductive ink is generally water or alcohol, which is hydrophilic and cannot be combined with non-hydrophilic substrate. Therefore, the substrate must be treated when fabricating FTCF. In addition to a single solvent, some binary solvents with different boiling points were chosen to reduce the surface tension. Chen et al. [36] selected a mixture of glycerol and ethylene glycol, composed of N-methylpyrroldione, glycerol, ethylene glycol and N-methylpyrroldione in the volume ratio of 1:(2–4):(5–7). Yu J et al. [37] prepared a high-viscosity alcohol-based silver nanowire conductive ink, which is composed of AgNWs with a mass fraction of 1.7%–3.8%, a UV-sensitive adhesive with a mass of 0.2%–0.7%, and a fluorocarbon surface with a mass of 0.008%–0.08%. Active agent, 0.5%–0.8% small molecule dispersant, 1%–4% mass small molecule levelling agent, 1%–3% mass small molecule humectant, 1.5%–2.5% small molecule defoamer, and the mass fraction is 85.12%–94.092% organic alcohol solvent. Chen et al. [38] dispersed 5 mg·mL⁻¹ of AgNWs in DMF to make AgNWs ink. Sato et al. [39] dispersed the nanowires in a mixed solvent of water and ethanol, and the mass ratio of water to ethanol was 70:30–99:1. In a liquid medium containing hydroxyethyl methyl cellulose (HEMC) at 0.01%–1.0%. Sohn et al. [40] dispersed AgNWs in a 0.1 mg/mL water/ethanol co-solvent solution (volume ratio 70:30), and combined it with a hydroxypropyl methylcellulose (HPMC) as binder, and then AgNWs ink was prepared by mixing.

The preparation process of AgNWs ink is relatively simple. Generally, AgNWs are directly added to the solvent, fully stirred, and then the binder and appropriate additives are added into AgNWs solution. Under normal circumstances, AgNWs in ink tend to precipitate and agglomerate. How to improve the stability of AgNWs inks has been a problem that researchers have been trying to solve. Binders cannot only improve the adhesion between AgNWs and substrate, but also adjust the viscosity and surface tension of ink, so as to adjust the printing adaptability of ink; surfactant with dispersing AgNPs or AgNWs to increase the wettability and durability and stability of ink; leveling agent increase the fluidity of ink. Mou et al. [34] reported a stable active silver ink composed of isopropanolamine silver complex, formic acid reducing agent and hydroxyethyl cellulose adhesive, which is used to make flexible electrodes. Using ultra long AgNWs (about 75 μm in length) as the conductive phase, Li et al. [35] developed AgNWs ins with simple formulation and fabricated FTCF with excellent conductivity (up to 8.32 × 10⁴ S/cm) and mechanical stability and light transmittance of about 80% on the flexible polyethylene terephthalate substrate by screen printing process, as shown
in Figure 3. Common binders include hydroxyethyl cellulose (HEC), hydroxyethyl methyl cellulose (HEMC), hydroxypropyl methyl cellulose (HPMC), etc. The dispersants may improve the dispersion and uniformity of AgNWs in solvent and improve the stability of ink. The dispersing and stabilizing mechanisms of dispersants mainly include the steric hindrance effect and electric double layer effect. The steric hindrance effect mainly depends on the polymer adsorbed on the surface of AgNWs to form a protective layer; the electrical double layer effect mainly depends on electrostatic repulsion to maintain the stability of AgNWs.

![Figure 3](image.png)

**Figure 3.** Images of the AgNWs ink and the corresponding screen-printed lines (Top: AgNW-inks. Bottom: screen-printed Ag NW lines.) with the water content x of (a) 1.0, (b) 1.5, (c) 1.8, (d) 2.0 g (AgNWs:cellulose:water = 0.4:0.4:x). Reprinted with permission from [35]; Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

To achieve stable droplet formation and the final printed shape in the printing process, the viscosity and surface tension of the ink formulation must be carefully tailored [31–36]. As we all know, the viscosity and surface tension of the ink are closely related to the concentrations and properties of AgNWs and additives. Surface tension caused by an imbalance of forces on the surface atoms is one of the important parameters affecting the printability and pattern accuracy of ink printing. The atoms on the surface of an object are different from those inside. Surface atoms are sparse and attractive to each other. For example, the droplets in space are in a state of weightlessness and can easily aggregate into a ball. When liquid drops are placed on the plate, the difference in surface tension results in the Marangoni flow; that is, the liquid flows from the low surface tension to the high surface tension. It is the presence of surface tension that leads to the coffee ring effect in screen printing and inkjet printing. During the drying process, AgNWs droplet edges become pinned to the substrate, and capillary flow outward from the centre of the drop brings suspended AgNWs to the edge as evaporation proceeds. After evaporation, suspended AgNWs are left highly concentrated along the original drop edge, resulting in non-uniform deposition of AgNWs. Therefore, how to handle the coffee ring effect caused by surface tension of conductive ink is troublesome. Until now, there are several ways to diminish the coffee ring effect: (1) increasing the amount of solute; (2) printing ink with a high contact angle; (3) adding surfactant; (4) using binary solvents with different boiling points [19]. Surfactant cannot only enhance the flow of Marangoni, but also reduce the liquid’s outward capillary flow. In addition, in order to obtain high quality FTCF, the surface tension should be controlled under $7 \times 10^{-2}$ N/m and different printing methods correspond to specific surface tension values [41,42].

3. Method of Printing

3.1. Gravure Printing

Gravure printing, as a promising electronic technology for large-scale printing, has been an important technology in recent years. All the printing patterns and characters are concave in the printing plate, as shown in Figure 4. It is widely used because of its fast speed, high quality, and ability to produce images of any shape. Each year a large number of packaging papers and plastic bags are
produced through the gravure printing process. In addition, gravure printing technology is also used to fabricate ceramic mesoporous films, perovskite solar cells, lithium-ion batteries, etc.

Herzog et al. [43] prepared ultra-thin mesoporous films with high uniformity by continuously printing two different “inks” and the experimental results showed that the preparation method of intaglio printing was much faster than that of the mesoporous monolayer and multilayer with traditional dip coating. Kim et al. [44] fabricated the flexible perovskite solar cells (PSCs) by gravure printing. The printing ink formulation and process parameters were optimized to make the film smooth and uniform, so the calcium titanium deposit was successfully formed. Montanino et al. [45] proposed a kind of Li-ion rechargeable printing battery based on LiFePO4 (LFP). Li et al. [46] obtained the organic-inorganic nanocomposites by incorporating the amphiphilic polymer precursor functionalized by alkoxysilane into the silica titanium dioxide hybrid network, thus successfully adopting the gravure printing method to prepare the flexible and transparent film with AgNWs and graphene.

Figure 4. Gravure printing method.

However, AgNWs-based FTCF fabricated by gravure printing technology is limited in resolution and electrical conductivity, which can be improved by adjusting related parameters, such as rheological property, viscosity, surface tension, and printing speed of conductive ink. Huang et al. [47] reported that they fabricated the AgNW pattern with resolution of up to 50 microns and the conductivity up to 5.34 × 10^4 s·cm⁻¹ on a flexible substrate by using gravure printing method. Peng et al. [22] reported that they prepared a transparent triboelectric sensor array by using the gravure printing method with AgNWs ink as printing materials. The printed electrode on the same film can collect the triboelectric induction signal independently without mutual interference.

3.2. Screen Printing

The screen printing process is suitable for almost all types of substrates and is widely used in textile, electronics, ceramic, glass, and other fields [47–51]. The screen printing process is shown in Figure 5a, the multi-mesh structure on the screen printing plate under the action of the scraper, the AgNWs ink may pass through the holes of the plate, so as to obtain one or more AgNWs film layers on the substrate. Abundant electronic devices were fabricated successfully via screen printing. Due to its good patterning function, screen printing technology is easy to realize the ordered connection and integrated fabrication of small area battery components.

Screen printing conductive ink is generally a pseudoplastic fluid, with shear thinning, shear failure, shear recovery flow characteristics. Its rheological properties have great influence on the adaptability of printing. The main influencing factors include conductive ink viscosity, fluidity, plasticity, and surface tension. Among them, the viscosity and the surface tension are the main factors affecting the adaptability of printing. High-viscosity ink easily leads to congestion, drawing, or even to not be transferred to substrate; low-viscosity ink tends to cause ink leakage, poor printing accuracy,
and printing patterns spreading each other. Therefore, the appropriate viscosity range is 14,000 to 12,000 mPa-s.

![Figure 5. (a) Screen printing method process, (b) Schematic diagram of the AgNWs ink preparation process and TSSs fabrication process by screen printing. Reprinted with permission from [49]; Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA. (c) the process of patterning AgNWs by combining screen printing and vacuum filtering. Reprinted with permission from [52]; Copyright 2020 American Chemical Society.](image)

Du et al. [48] reported that they printed water-based silver nanowire conductive ink on cotton fabric substrate by screen printing technology. Luo et al. [49] prepared a high-performance textile strain sensor by transferring the silver nanowire ink to the stretchable fabric through one-step screen printing, as shown in Figure 5b. Li et al. [51] prepared the super-capacitor with the landmark volumetric energy density of 18.8 mWh/cm$^3$ and the power density of 40.9 W·cm$^3$ by screen printing with the thixotropic hybrid ink of ruthenium oxide (RuO$_2$ × H$_2$O)–AgNWs–graphene oxide (GO) as in-plane microelectrode.

Screen printing is also a common method for many researchers. Kabir et al. [53] developed an electrochemical phosphate sensor by using a new type of screen printing electrode (SPE) modified by ammonium molybdate/silver nanowires (AMT/AgNWs), which realized the convenience, high sensitivity, wide detection range, high repeatability, and portability of phosphate detection. The sensitivities of SPE without AgNWs and with AgNWs/AMT were 0.1 and 0.71 µA/µm, respectively. Lin et al. [52] introduced a simple and effective method of making AgNWs network graphics by combining screen printing with vacuum filtering, as displayed in Figure 5c. The screen printed PDMS mask layer and the filter film were firmly combined to form a clear edge of AgNWs pattern with a resolution of 50 µM. The patterned thin films with a low density of AgNWs (<15 µg/cm$^2$) were transferred to the surface of PDMS, and the patterned transparent conductive films (TCF) were prepared. In addition, resolution of the pattern is closely related to mesh size, density, and conductive ink performance.
3.3. Inkjet Printing

Inkjet printing is widely used in the manufacture of electronic devices such as patch antenna, circuit board, biochemical sensor, frequency selection surface, etc. As shown in Figure 6, the printed conductive film can realize the graphic, large-scale, high efficiency, and low cost. Herein, inkjet printing is promising in flexible and stretchable electronic devices, such as transparent electrodes [54], paper-based semiconducting surface-enhanced Raman spectroscopy (SERS) substrates with two-dimensional MoO$_{3-x}$ nanosheets ink [55], electrochemically reduced graphene oxide microelectrodes [56], thin-film transistors (TFT) by inkjet etching method [57], and disposable electrodes with AgNPs-ink [58].

![Figure 6. Principle of inkjet printing.](image)

Micro-electronic ink-jet printers are used to print special patterns. The quality of conductive film can also be determined by the quality of printing equipment. The larger the nozzle size, the less likely it is to clog. Nevertheless, the large nozzle is not suitable for high printing resolution. The quality of the ink box and nozzle are two of the important standards to test the performance of inkjet printing equipment. However, so far, the technology of preparing high quality AgNWs-based FTCF by inkjet printing is not very mature, and it is still in the initial stage of exploration. Problems such as nozzle blocking and printing pattern breaking have not been effectively solved. Furthermore, the quality of the product may be slightly lower than that of the previous mature process. To some extent, ink-jet printing can simplify the processing steps and save the preparation time. Rao et al. [59] printed silver ion and pyrrole ink as catalytic layer and electroless plated Ni on the surface of polypropylene film, which reduced the time of mere electroless plating. In many cases, it is necessary to print several times to improve the conductivity, but this often leads to the decrease of light transmittance.

Table 1 lists the advantages and disadvantages of gravure printing, screen printing, and inkjet printing. These three printing methods can obtain graphics. However, since gravure printing is mainly used in the production of packaging paper, there is currently little research on conductive inks with gravure printing, and inkjet printing can easily block the nozzles, so the screen printing with AgNWs ink is now more researched.

In addition to gravure printing, screen printing, inkjet printing and other printing techniques, the researchers are constantly exploring new preparation technologies. So far, a large part of the printed AgNWs has been applied to the devices. Table 2 lists the current printing technology and application research status of AgNWs. In particular, screen printing is used more frequently, and inkjet printing is still under investigation.

<table>
<thead>
<tr>
<th>Printing Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravure printing</td>
<td>• Suitable for mass printing, mostly used for mass printing packaging paper; • Wide range of substrates, can be printed on paper, film, aluminum foil; • Good quality, thick ink layer; three-dimensional.</td>
<td>• A lot of ink is needed; • It is not suitable for short version products because of its high cost; • Can only be printed on flat substrates.</td>
</tr>
</tbody>
</table>
Table 1. Cont.

<table>
<thead>
<tr>
<th>Printing Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen printing</td>
<td>• Not limited by the size and shape of the substrate, screen printing can only print on hard objects, but also on soft objects; • Strong adhesion; • Convenient plate making, low price, easy to master technology; • Not only can be printed on flat surfaces, but also on curved, spherical, and concave-convex substrates; • Large area printing is possible; • Many types of inks can be used.</td>
<td>• The printing lines are thick, and fine patterns cannot be printed.</td>
</tr>
<tr>
<td>Inkjet printing</td>
<td>• Wide range of substrates, printing on paper and flexible substrates; • It’s easy to control the shape of the graph; • Well-designed technique for micro scale patterning of metallic nanomaterials.</td>
<td>• Nozzle is to blocking; • Printing speed is slow; • Low resolution, expensive print cartridge.</td>
</tr>
</tbody>
</table>

Table 2. The applications of Ag NW printings.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Printing Method</th>
<th>Devices</th>
<th>Substrate</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNWs</td>
<td>Gravure printing</td>
<td>Flexible Perovskite Solar Cells</td>
<td>-</td>
<td>Resolution = 50 μm; conductivity = 5.34 × 10⁴ S/cm</td>
<td>[47]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Aerosol jet printing</td>
<td>Transparent electrode of wearable devices</td>
<td>Glass</td>
<td>$R_s = 57.68 \Omega/ sq$, $T = 72.3%$</td>
<td>[60]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Direct Printing</td>
<td>Stretchable Sensor; LED</td>
<td>Si wafers, glass slides or polyimide films</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Electrohydrodynamic (EHD) jet printing</td>
<td>Electrode</td>
<td>Polyethylene terephthalate (PET)</td>
<td>$R_s = 45 \Omega/ sq$, $T = 90%$</td>
<td>[62]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>EHD jet printing</td>
<td>Transistor: source/drain (S/D) electrodes</td>
<td>SiO₂/Si</td>
<td>$I_{in}/I_{off} = 106$</td>
<td>[63]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Roll-to-Roll Printing</td>
<td>Electrode of solar cell</td>
<td>Polydimethylsiloxane (PDMS)</td>
<td>PCE = 3.04%</td>
<td>[64]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Inkjet printing</td>
<td>Bottom and top of electrodes of semitransparent organic solar cell</td>
<td>PEDOT:PSS</td>
<td>$R_s = 20 \Omega/ sq$</td>
<td>[65]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Screen printing</td>
<td>Electrode</td>
<td>PET</td>
<td>$R_s = 1.1$–$9.2 \Omega/ sq$, $T: 75.2%$–$92.6%$</td>
<td>[66]</td>
</tr>
<tr>
<td>AgNWs/silver flake</td>
<td>Screen printing</td>
<td>Strain sensor</td>
<td>Polyurethane</td>
<td>-</td>
<td>[67]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Screen printing</td>
<td>Antenna</td>
<td>PET</td>
<td>$R_s = 8.5 \Omega/ sq$, $T = 85%$</td>
<td>[68]</td>
</tr>
<tr>
<td>PEDOT:PSS/AgNWs</td>
<td>Screen printing</td>
<td>Heater</td>
<td>PET</td>
<td>$T = 85.6%$</td>
<td>[69]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Screen printing</td>
<td>Stretchable fabric electrodes</td>
<td>Textile</td>
<td>$R_s = 1.5 \Omega/ sq$</td>
<td>[70]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>Vacuum-free transfer-printing</td>
<td>PLEDs</td>
<td>ITO glass</td>
<td>Maximum device efficiencies of 3.81 cd/A</td>
<td>[5]</td>
</tr>
</tbody>
</table>

4. Flexible Transparent Conductive Film

Many experiments [69,71–73] have shown that the more AgNWs content of FTCF printed with AgNWs ink, the better the conductivity, but increasing the AgNWs content will reduce the light transmittance of FTCF, which is related to the conductive mechanism of FTCF. The relationship between light transmittance and conductivity of FTCF can be expressed by a formula that is simulated by the percolation theory adopted by De and coworkers [74].


FTCF can be applied in many electronic devices, such as the bottom and top electrodes of solar cells, and the electrodes of transparent heaters, touch panels, and sensors. The following is a brief introduction and analysis of these applications.

4.1. Solar Cells

In recent decades, solar cells have been a hot topic in the fields of energy and materials. Common performance parameters include open circuit voltage, short circuit current, filling factor, and power conversion efficiency. To some extent, the collection charge and transparency of flexible transparent electrodes directly determines the photoelectric conversion efficiency of solar cells. It is usually used as a transparent electrode, but indium is a rare metal, which is very expensive. The toxicity of indium is greater than that of lead [75,76]. The preparation process is complex and the conductivity on flexible substrate is poor, which hardly meets the performance requirements of flexible devices [77,78]. After integrating many factors, researchers will find low-cost and non-toxic materials that can partially replace ITO. AgNWs has excellent conductivity and light transmittance on flexible substrate, and the preparation process is simple. Therefore, AgNWs are often considered when making transparent electrodes of solar cells.

Thomas et al. [1] embedded AgNWs in a transparent conductive polymer poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) to change the nanowire structure and significantly enhance its conductivity, as shown in Figure 7a. Han et al. [79] processed semi-transparent perovskite solar cells with spray-coated AgNWs/ZnO composite top electrode, power conversion efficiency of 7.30% with an average visible light transmittance (AVT) of 23.3%, and with Rs of 78 Ω/sq, as shown in Figure 7b.

![Figure 7. (a) AgNWs embedded in PEDOT: PSS. Reprinted with permission from [1]; Copyright 2018 American Chemical Society. (b) Schematic structure of the devices with spray coated top AgNWs. Reprinted with permission from [79]; Copyright 2018 Elsevier.](image)

Performances of AgNW-based solar cells in recent years are listed in Table 3. In most of them, PEDOT:PSS is a promising conductive polymer, and PEDOT:PSS with AgNWs can get high PCE of 13.53%, which is relatively higher than that of the top electrode of the same AgNWs composite material. The roles of the top and bottom electrodes of solar cells are that sunlight penetrates and collects electrons, respectively. It is necessary to pass through more light as much as possible and collect the transition electrons quickly in a short time to improve the photoelectric conversion efficiency. Therefore, optimizing the conductivity and transmittance of the electrodes is very important.
The resistances to AgNWs conductive networks includes the resistance of AgNWs itself and the contact resistance of the junctions. There are several ways to reduce the contact resistance: thermal annealing, electrical annealing, mechanical pressing, plasma treatment, and illumination. But each has its drawbacks. For example, thermal annealing is not suitable for heat sensitive substrates; electrical annealing requires precise control of Joule heating and time to avoid AgNWs degradation; the required destructive mechanical pressure is not suitable for most plastic substrates; and expensive plasma treatment and lighting equipment. Later, the automatic welding of joints was gradually investigated. Lee et al. [87] introduced a method to realize spontaneous and selective welding of AgNWs junctions by electrochemical Ostwald ripening and high electrostatic potential, as shown in Figure 8a.

Huang et al. [17] used the capillary force and negative chemical potential at the AgNWs junctions to induce the selective epilayer growth of AgNWs at the nanowire junctions instead of its surface, which improved the stability and conductivity without reducing the transmittance, as shown in Figure 8b. Yang et al. [88] studied the sintering process of flash lamps. Under the optimal sintering process conditions, the resistance of AgNWs networks was reduced by about 20%. This convenient and fast welding process for AgNWs networks provides an opportunity for the mass production of AgNWs.

Table 3. Performance of AgNW-based solar cells.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>rGO/AgNWs/rGO</td>
<td>860</td>
<td>9.49</td>
<td>58.65</td>
<td>4.79</td>
<td>[80]</td>
</tr>
<tr>
<td>ITO/AgNWs/ITO</td>
<td>540</td>
<td>22.7</td>
<td>50</td>
<td>6.1</td>
<td>[81]</td>
</tr>
<tr>
<td>AgNWs/Gr/GO</td>
<td>550</td>
<td>20.00</td>
<td>63</td>
<td>8.68</td>
<td>[82]</td>
</tr>
<tr>
<td>AgNWs/TiO$_2$</td>
<td>727.4</td>
<td>19.8</td>
<td>67.6</td>
<td>9.74</td>
<td>[83]</td>
</tr>
<tr>
<td>TiO$_2$/AgNWs/TiO$_2$</td>
<td>940</td>
<td>19.35</td>
<td>69</td>
<td>12.55</td>
<td>[84]</td>
</tr>
<tr>
<td>AgNWs/Graphene</td>
<td>829</td>
<td>23.20</td>
<td>69.82</td>
<td>13.44</td>
<td>[85]</td>
</tr>
<tr>
<td>PEDOT:PSS/AgNWs</td>
<td>639</td>
<td>32.7</td>
<td>73.4</td>
<td>15.3</td>
<td>[86]</td>
</tr>
</tbody>
</table>

Figure 8. (a) Ag$^+$_ ions diffused from the AgNPs were reduced to Ag solders selectively at the junctions of crossing AgNWs. Reprinted with permission from [87]; Copyright 2018 American Chemical Society; (b) Reduction of Ag$^+$_ ions on the nanoscale and self-limited Ag deposition at the junctions. Reprinted with permission from [17]; Copyright 2019 American Chemical Society.
irregular pattern have an enhanced optical transmittance (~98.5%) and electromechanical stability (ΔR/R₀: ~42.4% at 200,000 cycles) under 6.7% strain.

It is also important to increase the light transmittance. The smaller the diameter of AgNWs, the lower the probability of photons colliding with AgNWs, which means that fewer photons are scattered or absorbed. In addition, the distribution of nanowires on the substrate also affects the light transmittance. The light transmittance is inversely proportional to the area density of conductive nanowires. As the mass fraction of AgNWs increases, the light transmittance will gradually decrease. The surface can be made into an eagle-eye structure or coated with an anti-reflection coating.

4.2. Transparent Film Heater

Transparent film heater (TFH) is a kind of temperature regulator. As an effective physical therapy, wearable hyperthermia is widely used to relieve pain caused by joint injury and to improve local blood circulation. Due to direct contact with human skin, it must have good flexibility, fit, excellent thermal efficiency, and heat resistance. At present, a large number of researches on TFH mainly focus on the following aspects: good flexibility, a higher steady-state temperature (Tₛ), fast heating response, and low working voltage. Some performances of AgNWs-based heaters in recent years are listed in Table 4. Through comparing those materials, AgNWs/AZO is a promising composite that can attain a temperature of over 100 °C with high transmittance of 93.7% [91]. Furthermore, Ni and NiO can significantly increase the Tₛ of naked AgNWs. Generally, Tₛ increasing is consistent with increasing of voltage, so getting low voltage and high Tₛ is an issue of TFH.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Substrate</th>
<th>Voltage (V)</th>
<th>Tₛ (°C)</th>
<th>$R_s$ (Ω/sq)</th>
<th>T (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/AgNWs</td>
<td>cPI</td>
<td>7</td>
<td>185.5</td>
<td>15</td>
<td>77</td>
<td>[92]</td>
</tr>
<tr>
<td>GZO/AgNWs/GZO</td>
<td>cPI</td>
<td>6</td>
<td>176</td>
<td>14.6</td>
<td>79</td>
<td>[93]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>PET</td>
<td>6</td>
<td>145</td>
<td>3.7</td>
<td>82.5</td>
<td>[17]</td>
</tr>
<tr>
<td>AgNWs/Ni</td>
<td>Quartz</td>
<td>10–30</td>
<td>284.3</td>
<td>13</td>
<td>82.8</td>
<td>[94]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>cPI</td>
<td>15</td>
<td>150</td>
<td>20</td>
<td>85.2</td>
<td>[95]</td>
</tr>
<tr>
<td>AgNWs/GO</td>
<td>PET</td>
<td>5.5</td>
<td>124</td>
<td>60</td>
<td>86</td>
<td>[96]</td>
</tr>
<tr>
<td>SiO₂/cPI/AgNW</td>
<td>Glass</td>
<td>6</td>
<td>105</td>
<td>17</td>
<td>86.9</td>
<td>[97]</td>
</tr>
<tr>
<td>AgNWs/AZO</td>
<td>PET</td>
<td>3</td>
<td>&gt;100</td>
<td>29.7</td>
<td>93.7</td>
<td>[91]</td>
</tr>
</tbody>
</table>

Compared with bulk silver, the melting point of AgNWs is very low. In the heating work, it is likely to melt, resulting in structural damage and out of work, how to improve the stability of the heater is very important. Goak et al. [98] fabricated SWCNT/AgNWs heater, with hybrid structure enhancing the long-term working stability and improving heating temperature. Figure 9a shows thermo reflectance images of the AgNWs (left) and SWCNT/AgNWs (right) films, and Figure 9b displays temperature time curves of the AgNWs and SWCNT/AgNWs heaters. The improved thermal stability of the hybrid heater was ascribed to thermal uniformity, in turn with regard to fast heat dissipation through heat transfer pathways of the serried SWCNT film, which delayed deformation and disconnection of AgNWs. Similarly, stability should be considered with fabricating. Shi et al. [99] fabricated a highly stable and TFH, through a simple drop-coating approach with burying AgNWs between colorless polyimide (cPI) and polymethyl methacrylate (PMMA), higher stability with the resistance increasing by 17% only for the initial value of 9.6 Ω after accelerating test at 105 °C and 100% relative humidity for 36 h. Wang et al. [93] fabricated flexible TFHs with a sandwich structure composed of Ga-doped ZnO (GZO) and AgNWs on the cPI substrate.
The electrodes of solar cells and TFH require a large adhesion between AgNWs and substrate, which can maintain the normal working state of the device and ensure the service life of the device. Most substrates have weak adhesion to conductive ink, which requires additional processing or other auxiliary materials as a transition. For example, ozone plasma or piranha solution treatment is used to make the substrate with oxygen-containing functional groups. Yang et al. [100] improved the bond strength with AgNPs ink by using the high force of Ag-S chemical bond. The thiol modified nanofiber cellulose was used as the substrate, which had excellent optical properties (−85% @ 550 nm) and ultra-small surface roughness (3.47 nm). It can actively attract AgNPs and combine them firmly, so that the conductive ink can print without ink adhesive, while even after large area peeling and bending, it can maintain high conductivity. This work may bring new opportunities for the manufacture of high-performance flexible electronic devices using the newly developed nano paper substrate.

4.3. Optoelectronic Devices

Optoelectronic devices are ubiquitous and have been integrated into human life, such as PLED and OLED. It is widely used in scientific research fields, such as near infrared detector, photoelectric conversion automatic control instrument, and an optical fiber communication receiving device. The transparent electrode prepared by AgNWs has excellent photoelectric properties, including threshold voltage, maximum current efficiency and Maximum luminous intensity. Performance of AgNWs-based optoelectronic devices in recent years are listed in Table 5. Recently, some researchers devoted to another kind of OLED. For instance, Kim et al. [4] fabricated fluorescent blue OLED by using AgNWs anode on a polyethylene terephthalate (PET) substrate. And Figure 10 shows a flexible OLEDs by Triambulo et al. [101]. From Table 5, we can see that the maximum luminous intensity of AgNWs used as OLED electrodes can reach 27,310 cd/m². AgNWs can be combined with materials with high light transmittance to increase the injection current and thereby increase the luminous intensity of OLEDs.

Table 5. Performance of AgNW-based optoelectronic devices.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Substrate</th>
<th>Area (cm²)</th>
<th>Threshold Voltage (V)</th>
<th>Maximum Current Efficiency (cd/A)</th>
<th>Maximum Luminous Intensity (cd/m²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNWs</td>
<td>Polymethyl methacrylate/PET</td>
<td>0.3 × 0.3</td>
<td>2.8</td>
<td>22.554</td>
<td>157</td>
<td>[102]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>PEDOT:PSS</td>
<td>-</td>
<td>3</td>
<td>17.90</td>
<td>1060</td>
<td>[103]</td>
</tr>
<tr>
<td>AgNW/ITO</td>
<td>PI</td>
<td>1 × 1</td>
<td>-</td>
<td>7.7</td>
<td>5000</td>
<td>[101]</td>
</tr>
<tr>
<td>Polyvinyl alcohol/AgNWs</td>
<td>Polyethylene terephthalate</td>
<td>-</td>
<td>10</td>
<td>35.3</td>
<td>18,540</td>
<td>[104]</td>
</tr>
<tr>
<td>AgNWs</td>
<td>glass</td>
<td>4 × 4</td>
<td>5.5</td>
<td>45.99</td>
<td>27,310</td>
<td>[105]</td>
</tr>
</tbody>
</table>
Figure 10. s-AgNW- and l-AgNW-type flexible OLEDs. Reprinted with permission from [101]; Copyright 2019 Elsevier.

4.4. Touch Panel

Touch panels are a new type of computer input device, which greatly enriches human life. The research of using AgNWs in touch panel is less than that of solar cell, heater and photoelectric device. But it is also a very promising application field, having the advantages of high transmittance, high conductivity, large size, low cost, and high flexibility. It is easy to prepare a small-area AgNWs touch panel in the laboratory. Nowadays, researchers pay more attention to large-area and good performance AgNWs touch panels. For devices used for long periods, cracks are easily formed. For example, Yang et al. [3] prepared a transparent touch screen with an area of $7 \times 7 \text{cm}^2$ by the Mayer rod coating method, with AgNWs/PEDOT:PSS as the top and bottom electrodes. And FTCF with sheet resistance of $12 \Omega \cdot \text{sq}^{-1}$ and transmittance of 96% at 550 nm was fabricated. After 100 times with friction or 5000 times bending, it can still be maintained and can work normally 2000 times or 24 h after working on a non-plane. Unlike solar cells and optoelectronic devices, the research focus in this field is mainly to improve the mechanical strength. Huang et al. [106] fabricated a transparent conductive film containing AgNWs-FTCF through RTR slit die coating and subsequent calendering process, and applied it to a resistive touch screen, displayed in Figure 11a–c. AgNWs is suitable for the preparation of touch panels due to its high light transmittance. The intensity of light transmittance directly affects the visual effect of the touch screen, so it is important to control its light transmittance. In addition, in order to enhance the anti-vertigo effect, the haze value of the AgNWs film should be reduced as much as possible.

Figure 11. (a) AgNW-SiO$_2$-based touch panel, (b) Writing on touch panel, (c) Letters written. Reprinted with permission from [106]; Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

4.5. Sensor

Almost all sensors have the following five requirements: excellent mechanical property, stability, high sensitivity, fast response time, and short recovery time. AgNWs has the highest conductivity and thermal conductivity in metal nanowires, and has high oxidation resistance and corrosion resistance. AgNWs with a high aspect ratio still has excellent conductivity in bending, rolling, or twisting. Therefore, there are many researches on AgNWs in all kinds of sensors.

Due to their excellent conductivity, AgNWs are used to fabricate strain sensors, which can be used to measure force, moment, pressure, acceleration, weight, etc. Zhang et al. [107] fabricated the AgNWs/MWCNT/thermoplastic polyurethane (TPU) fiber into a network structure, and prepared a
new type of weight strain fabric sensor, which can monitor the weight and shape of the object through the two-dimensional resistance change diagram, as displayed in Figure 12a,b. Zhu et al. [108] used the capillary method to integrate AgNWs into polyurethane (PU) fiber, and innovatively prepared a high sensitivity and stretchable millimeter diameter fiber strain sensor. Peng et al. [109] reported that a highly scalable sensor integrates capacitance and piezo-resistance mechanisms, which can simultaneously determine multiple forces.

Figure 12. (a) Fabrication of the weight-to-strain sensor based on free-written net structure. Reprinted with permission from [108]; Copyright 2019 American Chemical Society. (b) SEM images of Ag NW/MWCNT/TPU fibers. Reprinted with permission from [108]; Copyright 2019 American Chemical Society. (c) Compressive deformation of the pressure sensor under the external pressure. Reprinted with permission from [110]; Copyright 2019 American Chemical Society.

The pressure sensor with high sensitivity and wide pressure sensing range is an ideal choice for flexible electronic products. Gao et al. [110] developed a paper-based piezoresistive (APBP) pressure sensor with AgNWs as sensing material, nano cellulose paper (NCP) as bottom substrate of printed electrode and NCP as the top package layer. It is installed on human skin to monitor physiological signals of the human body (such as arterial pulse and throat pronunciation), as shown in Figure 12c. Zhu et al. [111] embedded gradient distribution AgNWs into PU mesopores, prepared a appreciable performance pressure sensor based on hybrid structure. This hybrid structure makes the PU/AgNWs pressure sensor with high sensitivity and wide detection range. Furthermore, Ding et al. [112] reported a multi-functional sensor with three-dimensional structure, which realized multi-modal detection of out-of-plane tactile stimulation and multi-directional non-contact environmental obstacle details. At the same time, the sensing behaviors of compression, stretching, magnetic field, sound wave, air flow, water level, water flow, and backwash are given.

Other types of sensors also use AgNWs. Luan et al. [113] developed an ultra-sensitive current-mode glucose sensor based on the synergistic effect of one-dimensional silver nanowires (AgNWs) and two-dimensional graphene sheets with high pore and three-dimensional nanostructures (3D NSS). He et al. [114] prepared a flexible and fast response humidity sensor, which was composed of alternating current electroluminescent devices (ACEL) and paper substrate ZnS:Cu. A phosphor layer was used as humidity functional part.

In addition to photoelectric performance of those devices, stability is also necessary for industrial applications. Although many different types of electronic devices have been successful in recent research, there are still few studies on their stability. There is little research on the aging mechanism of transparent electrodes in different environments, and an effective protective layer has not yet been formed. AgNWs devices are prone to failure or corrosion under service conditions, such as high temperature and bias. In optoelectronic devices, it is very important to ensure AgNWs electrodes that work normally for a long time. Stability includes chemical stability, electrical stability, mechanical
stability, and thermal stability. Methods to improve chemical stability include coating highly stable metal nanoparticles [115–117], metal oxides [118], graphene materials [119,120], and reducing the exposed area of nanowires to gases such as chemical vapor deposition graphene and reduced graphene oxide (r-GO); because graphene does not penetrate any gas chemically inert, it is commonly used to improve the stability of nano silver wire. Metals such as gold, nickel, palladium, or BN are used to form a core-shell structure to protect AgNWs from the external environment. Since the melting point of the nano silver wire is only a few hundred degrees Celsius, its thermal stability must be considered. It is possible to encapsulate a layer of material with a high melting point and good thermal insulation on the surface. For example, the dense structure of Al₂O₃ is not easy to penetrate oxygen, hydrogen sulfide and water molecules, and can simultaneously play a chemical protective role. Sohn et al. [40] mixed TiO₂ nanosheets (TiO₂ NS) and silver nanowires (Ag NW) networks to prepare flexible transparent conductive films (TCFs) with a light transmittance of 97% and a sheet resistance of 40 Ω/sq. The TiO₂ NS-Ag-NW hybrid TCF exhibits long-term chemical/aging and electromechanical stability. It is better than bare Ag-NW (ΔR_s/R_s > 4000%) or RuO₂-NS-AgNW mixture (ΔR_s/R_s > 200%).

5. Conclusions

AgNWs prepared by polyol method have excellent electrical conductivity and optical properties, and are a promising material to replace brittle ITO. In addition, graphene, carbon nanotubes, metal grids, and conductive polymers also have good electrical conductivity and light transmittance, and are commonly used in combination with AgNWs to obtain better performance FTCF. Recently, AgNWs appeared in flexible/stretchable/wearable electronic products. Also, today’s gradually developed printing technology has gradually realized large-area rapid preparation of low-cost flexible devices. The corresponding process is much simpler and more efficient than traditional ones. Therefore, the use of printing technology to prepare FTCF based on AgNWs is promising, which lays a solid foundation and provides opportunities for printing flexible electronic device technology in the future.

However, there are some problems that need to be solved urgently for printing AgNWs-based FTCF. First of all, there is a strong electromigration phenomenon in silver. Some other materials are combined with AgNWs to initially suppress this phenomenon, but this problem will still occur due to excessive current and even cause device failure. Second, there is a trade-off relationship between conductivity and transmittance. The conductivity of FTCF should be improved as much as possible without undue damage to the transmittance. Third, the electrical conductivity, light transmittance and stability of FTCF after compression, stretching, or twisting will deteriorate or even shorten its life. Finally, there are still problems such as poor rheology and poor dispersion of the conductive ink, so the printing process parameters should be optimized as much as possible. Many research results on printing AgNWs-based FTCF mainly achieved excellent performance in only one or two aspects, but the other performance was not good. Therefore, to develop more versatile technologies or methods to prepare FTCF, and in order to meet the needs of various aspects as much as possible, there is still a lot of work to be done.

6. Outlook

AgNWs itself has excellent electrical conductivity and light transmittance, and is the material of choice for a new generation of flexible electronic devices. Regarding the future development direction of printed AgNWs flexible devices, we can proceed from the following aspects: (1) Theoretically study the performance parameters of AgNWs ink, including rheological properties, micro-mechanism of reducing surface tension, and improving the dispersion and stability of its performance. (2) The photoelectric properties of only AgNWs may have been studied to the limit. More research should be done on how the properties of AgNWs change with other metal wires or metal oxides, so as to develop composite materials with better properties. (3) The problem of adhesion between AgNWs ink and substrate still needs to be improved, and a flexible film with high adhesion can be developed by combining theory and practice.
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