Flexible transparent electrodes (TEs) are important for new electronic devices. This paper reports a scalable, cost-effective Ag nanowires (AgNWs) TE, which is made of a SnO$_2$-xH$_2$O and AgNWs composite layer and a flexible polyethylene terephthalate (PET) bottom layer by a solution method at room temperature. The AgNWs/SnO$_2$-xH$_2$O composite TEs reveal a significant reduction of four orders in magnitude of sheet resistance, from 90 kΩ sq$^{-1}$ to 12 Ω sq$^{-1}$, while retaining transmittance of about 92% at 550 nm. This could be owing to the significant reduction of contact resistance for the weld-like junction of bound AgNWs. Compared with others, this method is characterized by filling gaps of the silver nanowire network with SnO$_2$-xH$_2$O. In addition, the adhesive forces between the AgNWs and the substrate are improved. This could be attributed to strong adhesion of SnO$_2$-xH$_2$O with the substrate. Moreover, this foldable transparent electrode is applicable for any non-planar surfaces and ultimately for future wearable optoelectronic devices.
easily solve the problem of electrical conductivity and fill the gap between nanowires. Whereas PEDOT:PSS severely limits the device lifetime, and most of the nanoparticles need high temperatures (140 °C to 250 °C). Zilberberg et al. use SnO2 sol-gel process to fabricate the TEs even at room temperature with the method of atomic layer deposition (ALD).23 But ALD limits the roll-to-roll production. So, currently, it still cannot achieve a large scale of cost-effective production.10,11,23

Thirdly, AgNWs TEs are easily to fall off the substrate due to the poor adhesion, which limits both of its usage and mass production. The composite electrode is very helpful to improve adhesion. However, the current technology is not suitable for roll-to-roll production.

In this work, we report a solution method to fabricate AgNWs TEs on PET substrate at room temperature which is suitable to the roll-to-roll production. More importantly, the fabrication processes are scalable and cost effective. With this method, the $R_{\text{th}}$ of the TEs can be reduced by four orders while maintaining high transmission. In addition, the gaps between the nanowires are successfully filled and the adhesion between the AgNWs and the substrate are improved. Moreover, this flexible transparent electrode is applicable for any flexible substrate and ultimately for future wearable optoelectronic devices. This will be of great significance to the extension and application of the electrode.

2. Experiment

2.1 Synthesis of AgNWs

The AgNWs were synthesised by salt-assisted polyol method (Fig. 1a). 30 mL ethylene glycol (EG) solution of 0.052 mol L$^{-1}$ AgNO3 and 0.067 mol L$^{-1}$ PVP was thoroughly agitated. Then, another 30 mL EG solution was prepared and heated at 130 °C for 1 h. 2.5 mL EG solution of $6 \times 10^{-4}$ mol L$^{-1}$ FeCl3 was dropped into the heated 30 mL EG. After 5–10 min, the mixed solution containing AgNO3 and PVP was added with a dropping speed of 0.5 mL min$^{-1}$ into the heated solution. Finally, post-reaction solution was cooled naturally and then filtered by qualified filter paper (intermediate speed). AgNWs were washed out of the filter paper with deionized water. AgNWs were obtained by centrifugation at speed of 2000 rpm. Then the precipitation was retained, and the solution was replaced by ethanol. The step of centrifugation was repeated for three times.

2.2 Fabricate of AgNWs TEs

AgNWs were ultrasonically dispersed in ethanol with the concentration of 0.35 mg mL$^{-1}$ (Fig. 1b). The AgNWs TEs were fabricated by the doctor-blade on the substrate of PET (Fig. 1c and d). Then the films were immersed in aqueous solution of SnCl4·5H2O (6% w) for 10 s. Finally, the TEs were washed with deionized water and dried.

3. Results and discussion

3.1 Conductivity

The $R_{\text{th}}$ of the AgNWs TEs without any post-treatment are as high as 90 kΩ sq$^{-1}$. This is a problem that AgNWs TEs usually have, mainly because AgNWs are piled up on the substrates without any contact. Therefore, the improvement of contact is very important for good conductivity. Fortunately, we found a scalable, and cost-effective way to solve this problem. The AgNWs TEs were immersed into the solution of SnCl4·5H2O (6% w) for 10 s. The $R_{\text{th}}$ of initial AgNWs TEs, SnO2·xH2O film and AgNWs/SnO2·xH2O composite TEs is shown in Fig. 2. The conductivity of the initial TEs is very poor with the $R_{\text{th}}$ over 90 kΩ (blue pillar). Similarly, the $R_{\text{th}}$ of the only SnO2·xH2O (red pillar) is 6 kΩ which is also too high for TEs. Fortunately, the $R_{\text{th}}$ of the AgNWs/SnO2·xH2O composite TEs (green pillar) is just 12 Ω sq$^{-1}$. The $R_{\text{th}}$ of AgNWs TEs was reduced dramatically from 90 kΩ sq$^{-1}$ to 12 Ω sq$^{-1}$ by 99% or about 4 orders of magnitude.

To found the cause of the increase in conductivity, we analysed the solution. The solution of SnCl4·5H2O is not stable and easy to hydrolyse. The reactions in the aqueous solution of SnCl4·5H2O can be expressed as:

\[
\text{SnCl}_4 + 6\text{H}_2\text{O} \rightarrow \text{H}_2[\text{Sn(OH)}_6] + 4\text{HCl}
\]

(1)

\[
\text{SnO}_2\cdot6\text{H}_2\text{O} + 6\text{HCl} \rightarrow \text{H}_2\text{SnCl}_6 + 8\text{H}_2\text{O}
\]

(2)

![Fig. 1](image1.png) 

Flow chart of AgNWs/SnO2·xH2O composite TEs. (a) Prepare AgNWs by salt-assisted polyol method; (b) disperse AgNWs in ethanol with 0.35 mg mL$^{-1}$ concentration; (c) Fabricate electrode by doctor-blade method; (d) initial electrode; (e) soaking treatment for 10 s; (f) schematic illustration of AgNWs/SnO2·xH2O composite TEs.

![Fig. 2](image2.png) 

$R_{\text{th}}$ of initial AgNWs TEs, SnO2·xH2O film and AgNWs/SnO2·xH2O composite TEs.
where $H_2[Sn(OH)_6]$ in eqn (1) can be written as $SnO_2\cdot 6H_2O$ which will react to HCl to obtain product $H_2SnCl_6$ that causes the solution to be acidic with pH value of 2, as confirmed through experiments. And because the number of $Cl^-$ is smaller than $Sn^{2+}$, there is still some residual of $SnO_2\cdot xH_2O$. As a result, the hydrolysis of the solution finally obtained the $SnO_2$ colloid and $H_2SnCl_6$.

There are two main effects of $SnCl_4\cdot H_2O$ solution on TEs, which lead to the $R_{sh}$ reduction of four orders in magnitude, from 90 k$\Omega$ sq$^{-1}$ to 12 $\Omega$ sq$^{-1}$.

Firstly, $SnO_2\cdot xH_2O$ can make the nanowire in close contact and fill the gap of AgNWs TEs. The nanowires will be adsorbed on the substrate due to the strong adhesion of $SnO_2$ with substrate. And adhesion of $SnO_2$ with glass can even reach 20 MPa. $SnO_2\cdot xH_2O$ can help the nanowires adhere firmly to the surface of the substrate and contact closely to each other for better transmission of electrons. Moreover, the filling of the voids by $SnO_2\cdot xH_2O$ is very important for electronic devices. The filling of the nonconductive voids can improve the collection of carriers which will improve the performance of electronic devices.

Secondly, $Cl^-$ ions could help to bind the AgNWs together and form a weld-like junction which will further increase the conductivity of the film. As discussed in previous studies,$^{21}$ silver atoms in AgNWs may be dissolved slowly in the presence of $Cl^-$ and dissolved oxygen in water. Due to redox reactions, it will produce solvated silver ions (Ag$^+$). The redox reaction can be written as:

$$4Ag + O_2 + 2H_2O \leftrightarrow 4Ag^+ + 4OH^- \quad (3)$$

We need to pay attention to the atomic oxygen on the silver surface. It may block the re-deposition of silver ions onto the silver surface. And atomic oxygen on the silver surface comes from molecular oxygen which is adsorbed and dissociated to atomic oxygen between 200 K and 500 K.$^{24}$ However, concentration of dissolved oxygen in water is very limited so that Ag$^+$ ions could redeposit onto the relatively more active AgNWs surface and junction. The deposition of Ag at the junction will allow the two nanowires to be successfully welded together and will reduce $R_{sh}$ which is the main source of $R_{sh}$. So, the $Cl^-$ in the solution can help improve the conductivity of TEs.

In Table 1, the electrical properties of different composite TEs are compared and analysed. The last row presents our results, whose perform is seen to be better than other types of electrodes. When the length of the nanowire is doubled, the resistance is reduced by an order of magnitude. In contrast, while the diameter varies at 50–100 nm, the transmittance is maintained at 90%, the longer the nanowires are, the better the electrical properties. And we also found that when the length is the same, the thinner the nanowire is, the better the electrical properties are.

### 3.2 Optical properties

Optical properties are also an important aspect of transparent electrodes. Fig. 3 shows the change of transmittance ($T$), scattering ($S$), and haze ($H$) properties of initial AgNWs TEs and AgNWs/SnO$_2\cdot xH_2O$ composite TEs. Haze is a percentage of the transmitted light intensity which is more than 2.5 degrees deviation from the incident light. And haze is equal to the percentage ratio of the scattered light flux ($S$) within large angles deviating from the incident direction by more than 2.5° to the transmitted luminous flux ($T$), i.e.

$$H = \frac{S}{T} \times 100\%$$

where $H$ represents haze, and $S$ represents the large-angle scattered light flux, and $T$ represents transmitted luminous flux. The demand for haze is not the same for different applications. For display devices, haze should be as small as possible.
Therefore, to reduce the resistance of the initial AgNWs TEs probably comes from the poor contact. Nanowires are even turned up. Accordingly, the large resistance arbitrarily. The contact between AgNWs is poor, and some of the nanowires are not lay flat on the substrate, but tilt arbitrarily. The contact between AgNWs is poor, and some of the nanowires are all compacted on the substrate and some nanowires are in good contact in AgNWs/SnO2·xH2O composite TEs.

3.3 Morphology

Fig. 4a and b are the diagram of structure of the initial AgNWs TEs. Fig. 4c and d are the SEM image corresponding to the schematic in Fig. 4a. From Fig. 4c, we can see that the length of AgNWs is about 10–20 μm, and the diameter is 50–100 nm. As shown in Fig. 4d, AgNWs do not lay flat on the substrate, but tilt arbitrarily. The contact between AgNWs is poor, and some of the nanowires are all compacted on the substrate and some nanowires are in good contact in AgNWs/SnO2·xH2O composite TEs.

Therefore, to reduce Rsh, we need to first reduce the Rs. Fig. 4b and e are the schematic and SEM image of the composite TEs, respectively. Fig. 4e shows that SnO2·xH2O filled the gaps between nanowires or even covered the surface of the nanowires. Fig. 4f is a SEM image of damaged composite TEs which was made on a flexible substrate and pulled to split. It is seen through the tearing film in Fig. 4f, the gaps in the nanowire are really filled by the material. Fig. 4e and f show that nanowires are all compacted on the substrate and some nanowires are in good contact in AgNWs/SnO2·xH2O composite TEs.

The junction of the composite TEs is tested by TEM to confirm the contact of the nanowires. Fig. 5a and b show the TEM images of the crossing structure of initial TEs and the composite TEs. For initial AgNWs TEs (Fig. 5a), the connection between the crossed AgNWs is not welded. And the force between the nanowires is mainly van der Waals force. For the AgNWs/SnO2·xH2O composite TEs, the connection between the crossed AgNWs is welded. The force of the weld-like junction is intermolecular force. Therefore, the nanowires are firmly and stably welded together although exfoliated by the ultrasonic from the substrate. This means that the solution of SnO2·xH2O can help to improve contact of nanowires.

3.4 Chemical analysis

The chemical in the nanowire gap is characterized. Fig. 6a shows the TEM-image of the film. Obviously, there is a layer of material, which might be amorphous, deposited onto the surface of the TE and AgNWs. Based on the analysis of the components of the hydrolysis solution, the amorphous substance on the film surface are believed to be SnO2·xH2O.

The elemental composition is determined by Energy Dispersive Spectrometer (EDS). Fig. 6c shows the EDS spectrum of the amorphous, and reveals the presence of tin (Sn), oxygen (O), carbon (C), copper (Cu) and chlorine (Cl) elements in the sample. Carbon is the most abundant. This could be attributed to the amorphous carbon-coated copper grids, which is also the source of copper. The small amount of chlorine comes from the H2SnCl6 in the solution. The most important thing is verifying the existence of tin and oxygen in the amorphous thought to be SnO2·xH2O. To further confirm our speculation, we need to remove the crystalline water from the amorphous to verify the existence of SnO2. When SnO2·xH2O is annealed at 400 °C for 30 min, SnO2·xH2O will be turned into the crystallized SnO2. The crystallized SnO2 is characterized by high resolution transmission electron microscopy (HRTEM). The HRTEM image shows a clear lattice spacing of 3.3 A in Fig. 6b, which exactly matches to the (110) plane of single crystal SnO2.

Fig. 6d presents the XRD patterns of this crystalline substance. The major XRD peaks at 2θ = 26.61, 33.89, 37.95, 51.78 and 65.94° are assigned to the (110), (101), (200), (211) and
(301) reflection planes of tetragonal SnO\(_2\), respectively. The diffraction peaks of the products can be well indexed to the known tetragonal rutile SnO\(_2\) (JCPDS 41-1445), which confirms the presence of SnO\(_2\) in the annealed products. So far, the amorphous material is determined to be SnO\(_2\)\(\times\)H\(_2\)O.

### 3.5 Thermal Stability

The thermogravimetric analysis of SnO\(_2\)\(\times\)H\(_2\)O shows that SnO\(_2\)\(\times\)H\(_2\)O began to severe loss of water from 100 °C (Fig. 7a). Nevertheless, crystallization temperature of SnO\(_2\) is about 400 °C. If SnO\(_2\)\(\times\)H\(_2\)O is heated at 100 °C or 200 °C, we will get the amorphous substance which removed some of the crystal water.

This simple heat treatment surprisingly gives us an unexpected benefit that the adhesion of the film is significantly improved. As we all know, the thin film of AgNWs can easily be erased when we touch it gently due to the poor adhesion of the initial AgNWs TEs. However, there’s always a way out! The adhesion of the composite TEs can be improved by heat treatment, and the TEs can also tolerate adhesive tape test.

XPS spectra are used to characterize the initial composite TEs and the heated composite TEs at 200 °C. We want to know whether the heat treatment has other effects on the electrode, in addition to the loss of crystalline water. Fig. 8 shows the X-ray photoelectron spectroscopy (XPS) of the composite TEs. The XPS survey spectrum (Fig. 8a) shows the peaks of Ag 3d doublet, Sn 3d doublet, Sn 4d and O 1s peaks. There are two peaks with binding energies of 368.3 eV for Ag 3d\(_{5/2}\) and 374.3 eV for Ag 3d\(_{3/2}\) in the regional spectrum (Fig. 8b) of Ag 3d. This is consistent with the standard binding energy of pure silver. The peaks at a binding energy of 486.6, 495.3 and 27.1 eV (Fig. 8c) can agree with the Sn 3d\(_{3/2}\), Sn
3d_{3/2} and Sn 4d_{3/2}, respectively. Their standard combination can be very close to the previously reported results, indicating that the valence states of Ag and Sn are 0 and +4, respectively. This means that the heat treatment at 200 °C does not cause a change in the valence of the composite electrode.

4. Conclusions

As reported previously, AgNWs transparent electrode usually has the problems of poor initial conductivity and intrinsic gap between nanowires. This paper demonstrated a simple solution-processed method for a scalable, cost effective and flexible AgNWs TEs. Compared with others, this method is characterized by the gap of the silver nanowire network filled by SnO_{2}·xH_{2}O. The electrode forms a new kind of AgNWs/SnO_{2}·xH_{2}O composite structure just with 10 s immersion in solution of SnCl_{4}·5H_{2}O at room temperature. It is confirmed that aqueous solution of SnCl_{4}·5H_{2}O could help to reduce the R_{sh} by four orders of magnitude, from 90 kΩ cm^{-1} to 12 Ω cm^{-1}, while keep transmittance of about 92% at 550 nm. In addition, the adhesive forces between the AgNWs and the substrate is improved. The optimization of the performance is attributed to the effects of SnCl_{4}·5H_{2}O solution which mainly contains Cl^{-} and SnO_{2}·xH_{2}O because of hydrolysis. There are two main effects on AgNWs TEs. Firstly, Cl^{-} can help to fuse the contact of nanowires which reduces R_{sh} of TEs. Secondly, SnO_{2}·xH_{2}O can help to fill the space of networks. The conductivity of the composite TEs is improved attributed to this important filling. At the same time, the coverage on the active areas can improve the efficiency of charge extraction/injection for devices. Surprisingly, the adhesion of AgNWs TEs can be significantly improved with 100 or 200 °C heating. What's more, the simple solution-method at room temperature makes it possible for the roll-to-roll production.

Conflicts of interest

There are no conflicts to declare.

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