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Coating-free, air-stable silver nanowires for high-performance transparent conductive film

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Abstract
Silver nanowire (Ag NW) based films are considered as a promising alternative for traditional indium tin oxide but still suffer from some limitations, including insufficient conductivity, transparency and environmental instability. We here report a novel etching synthesis strategy to improve the performance of Ag NW films. Different from the traditional methods to synthesize high aspect ratios of NWs or employ electrically conductive coatings, we find it effective to reduce the high-reactivity defects of NWs for optimizing the comprehensive performance of Ag NW films. In this strategy etching can suppress the generation of high-reactivity defects and meanwhile the etching growth of NWs can be accomplished in an uneven ligand distribution environment. The resulting Ag NWs are uniformly straight with a sharp-edged structure. The transparent conductive film obtained exhibits simultaneous improvements in electrical conductivity, transparency and air stability. Even after exposure in air for 200 days and no protective coatings, the film can still meet the highest requirement of practical applications, with a figure of merit 361 (i.e., FoM > 350). These results not only demonstrate the importance of defect control in the synthesis of Ag NWs, but also pave a way for further optimizing the performance of Ag NW-based films.

Supplementary material for this article is available online

Keywords: transparent conductive film, silver nanowires, etching synthesis, electrical conductivity, air stability

1. Introduction
Silver nanowires (Ag NWs) are important for portable electronics, energy conversion and flexible display [1, 2], however, their applications suffer from many limitations due to poor electrical conductivity and environmental corrosion. To this end, the ‘post-treatment’ strategy of Ag NWs networks has been employed to overcome these shortcomings, including constructing extra conductive paths [3, 4], joint fusion [5–8], surface coating [3, 9, 10] and so on. Nevertheless, it remains elusive how to simultaneously improve the transparency, conductivity and air stability of resulting films. In scalable polyol synthesis, the studies involving ‘pre-synthesis’ mostly concentrated on increasing the aspect ratio of NWs, given that the inherent structure of Ag NWs is the bearer of the final properties [11–13]. We here demonstrate a new strategy to improve the comprehensive performance of Ag NW films, through optimizing the high-reactivity defects of Ag NWs to significantly enhance the electrical conductivity and air stability without the need of additional surface coating layers.

Defects are ubiquitous in pentagon structure of face-centered cubic arrangement where perfect structure possesses...
a gap of 7.35° [14]. To fill the gap in generating closed structures, the defects have to occur in real Ag NWs with the pentagon structure (called intrinsic defects) [15, 16]. The synthesis of penta-Ag NWs is a process that continuously constructs penta-structures and hence continuously generates intrinsic defects. Besides the intrinsic defects, there exist two additional types of defects in resulting Ag NWs. One of them arises from the kinetic confinement in the rapid growth of NWs, and the other originates from the coalescence of different active seeds [14, 17]. The presence of these defects makes Ag NWs easy to be corroded environmentally and causes the break of NWs or pulverization, significantly lowering the electrical conductivity and air stability [18]. As a result, it is critical to optimize the crystal structure of NWs in the process of synthesis for optimizing the performance of transparent films.

Generally, the environmental corrosion or etching degradation of Ag NWs is inhomogeneous due to the existence of defect sites with different reactivities [17–19]. High-reactivity sites imply large crystal lattice strain or more lattice mismatches [17], which is the primary factor that causes lowered electrical conductivities or environmental instability. However, it remains challenging how to control or reduce the content of high-reactivity defects in Ag NWs. Intuitively, etching might be helpful for eliminating the high-reactivity defects, given their high sensitivity to oxidation media. Such etching effect has been exploited in the controlled growth of nanocrystals [20]. For instance, the etchant O2/Cl− or Br− was able to suppress the generation of multi-twined structures so that single crystal products resulted [21, 22]. Nevertheless, such etching effect has never been used in the synthesis of Ag NWs, because the penta-twined precursor of Ag NWs is not stable in etching environments [20, 21, 23].

We here demonstrate a novel synthesis method that exploits ‘etching effect’ to prepare few-defect Ag NWs, in which the formation of high-reactivity defects is suppressed due to the presence of uneven ligand distribution environments. In the liquid-phase synthesis, the ligand-rich aggregates contribute to protect the precursors of Ag NWs while the ligand-depleted regions allow the sustained growth of Ag NWs. The resulting Ag NWs (etching synthesis-generated Ag NWs, called SG-Ag NWs) are uniformly straight, with a sharp-edge structure. They are easy to be filtrated into transparent films that exhibit excellent optical, electrical properties and air stability, superior to those Ag NWs with higher aspect ratios. The SG-Ag NWs film reveals a sheet resistance as low as ∼10 Ω/sq, an optical transmittance of ∼93% (a haze factor of ∼7%), and a small increase (∼14 Ω/sq) after exposed in air for 200 days.

2. Methods

2.1. Synthesis of Ag NWs

2.1.1. Materials. Polyvinylpyrrolidone (PVP, K-30, \( M_w = 45\,000–58\,000 \)) , ethylene glycol (EG), ferric trichloride (FeCl₃), sodium chloride (NaCl), ferric nitrate (Fe(NO₃)₃), potassium nitrate (KNO₃) and silver nitrate (AgNO₃) were purchased from Sinopharm Chemical Reagent Company; PVP (\( M_w = 1300\,000 \)) was purchased from Sigma.

2.1.2. Process of preparing Ag NWs [11–13, 23–26]. 0.2 g PVP (K-30) and 0.2 g PVP (\( M_w = 1300\,000 \)) were added to a 100 ml vial containing 40 ml EG solution, which was heated to 130 °C under nitrogen atmosphere. After the PVP added completely dissolves, the \( N_2 \) stream sustain for another 10 min 6 ml FeCl₃ EG solution (0.1 mg ml⁻¹) was added, followed (1 min later) by AgNO₃ EG solution (0.5 g AgNO₃ in 10 ml EG dispersed by ultrasonic, the solution is transparent and colorless) via pipette (Dragonmed range 0–200 μl) at the rate 12.5 s/100 μl. After that, the reaction mixture was held at 130°C for 6 h (the whole process was operated under \( N_2 \) stream and continuous magnetic stirring). The final reaction solution was fast cooled down by ethanol, which had been frozen beforehand in ice-water bath, centrifuging three times in ethanol at 3000 rpm for 10 min, and then dissolved in ethanol for subsequent study. To track the reaction state, first, the mixture (5 ml) of different reaction time was sucked into deionized water (45 ml) equipped with an ice-water bath (within 30 s) to give the samples for TEM, SEM, UV–vis characterizations. Subsequently, the obtained solution was centrifuged twice at 12000 rpm for 10 min to give supernatant. Finally, the supernatant was filtrated twice using poly (phenylene oxide) membrane (PPO, pore diameter 0.22 μm) for inductively coupled plasma atomic emission spectroscopy (ICP AES) characterization.

2.2. Preparation of transparent films

Poly (vinylidene fluoride) membrane (PVDF, pore diameter 0.22 μm) was purchased from Shanghai Xinya company, and PDMS (SYLGARD 184) was purchased from Dow Corning company. The process of preparing Ag NWs transparent film is shown in figure S11, available online at stacks.iop.org/NANO/29/375601/mmedia. Firstly, Ag NWs ethanol dispersion was filtrated with a PVDF. Then, the PVDF membrane containing the Ag NW film was transferred onto a PET substrate via the following procedure. We first covered the surface of the PET substrate with enough ethanol and then placed the PVDF + Ag NWs membrane onto the ethanol liquid surface. With the volatilization of ethanol, the PVDF membrane was adhered closely to the PET surface. After ethanol was volatilized exhaustively, the PVDF membrane detached itself from the PET substrate and an Ag NW transparent film (diameter 40 mm) adhered on PET substrate was obtained. The same operation was also applied to PDMS substrate, besides an additional peeling step was used to remove the PVDF membrane. This film preparation process was applied in all Ag NWs in our experiment.

2.3. Instrumentation

 Ultraviolet and visible spectrophotometer (UV–vis) with integrating sphere accessory (Lambda750, Perkin-Elmer) was used to test the transparency of film (PET substrate as
reference, $\lambda = 550$ nm) and the surface plasma resonance of silver nanocrystal (water as a reference). Four point probe tester (ST2263, Suzhou Jingge Electronic Comp. Ltd) was used to detect the sheet resistance of film. X-ray diffraction (XRD), X’Pert PRO diffractometer (PANanalytical, 40 KV and 40 mA, monochromatic Cu Ka radiation ($k = 1.54 \text{ Å}$)), was used to examine the crystal lattice of the Ag NW powder. Thermogravimetric analysis (TGA, Mettler Toledo TGA 1) of all samples were performed from 100 °C to 600 °C at a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere. Field emission scanning electron microscope (FESEM, Ultra 55, Zeiss), transmission electron microscopy (TEM, Tecnai G$^2$ TF20 Twin, 200 kV), and atom force microscope (AFM Multimode 8, Bruker, tapping mode) were applied to observe the morphology and structure of Ag NWs. ICP-AES (Thermo Fisher Scientific, iCAP 7400) was used to determine the real amount of Ag$_{nm}^{n+}$ at the different reaction times.

3. Results and discussion

3.1. Etching synthesis-generated Ag NWs

The SG-Ag NWs are quite straight with a uniform, sharp-edged structure and an aspect ratio of ~500, as shown in figures 1(a)–(c) and S1(a)–(c), which agrees with the ideal penta-twinned structure, but significantly different from those previously reported results [24]. Owing to the etching effect and the reduction of high-reactivity defects, such Ag NWs are expected to show good anticorrosion capability or air stability. To illustrate this, we compare the anticorrosion capability of different Ag NWs that exposed in air for 24 days. For Ag NWs, oxidative corrosion is generally inevitable due to the presence of defects, especially for those containing high-reactivity defects. However, it is found that the extent of oxidative corrosion reduces with the decreased content of high-reactivity defects. Etching synthesis contributes to reduce the content of high-reactivity defects in Ag NWs and thus better corrosion resistance. As shown in figure 1(d), although some uniform nano-bumps appear on the surface of SG-Ag NWs after exposure for 24 days, no break points are observed in most SG-Ag NWs. By comparison, some break points are observed in two kinds of non-etching synthetic Ag NWs (that is, uniform or even ligand distribution synthesized product and commercial Ag NWs, see figures 1(e), (f) and their insets), which implies that the etching effect is effective for suppressing occurrence of high-reactivity defects and deep corrosion in oxidative environments. In addition, it was found that although PVP coatings on the Ag NW surface probably contribute to improve the air stability, the content of high-reactivity defects seems to be more critical, especially for suppressing the deep environmental corrosion or the occurrence of break points. According to the TGA results (figure S2(a)) and width of them (~80 nm, ~100 nm and ~20 nm respectively for figures 1(d)–(f), corresponding statistical distribution as seen from figure S3), the molar ratio between PVP units and surface Ag atoms for SG-Ag NWs was calculated to be 0.5 [27], which is 3 times less than those of two other Ag NWs (figure S2(b)). In other words, although PVP molecules cannot coat the whole SG-Ag NW surface, that is, less PVP protection or more contact between NWs and oxidative etchants, no visible deep corrosion or break points occur. Apparently, such an etching synthesis strategy opens a promising door to further improve the comprehensive performance of Ag NWs.

3.2. Etching effect in Ag NWs synthesis

The growing environment of etching synthesis requires more ligand molecules in the nucleation stage to protect active precursors but the growth stage requires relatively less ligand molecules to ensure the etching effect. Different from the existing synthetic methods, we constitute such growing environment through a locally uneven ligand distribution at high ligand concentrations. Typically, a PVP mixture was dissolved in EG forming a uniform ligand solution (90 mmol l$^{-1}$), to which silver nitrate (AgNO$_3$) EG solution was added slowly (figures 2(a), (b)). In this process, Ag$^+$. ions first added prefer to coordinate with excess repeating units of PVP [25, 26]. Once the coordination is established, the restricted chain motion of PVP will suppress the coordination between additional Ag$^+$ ions and the repeating units. This implies that those Ag$^+$ ions first added can form ligand-rich aggregates while those Ag$^+$ ions added later have to keep in PVP-deficient regions, resulting in a solution structure with uneven ligand distributions that is beneficial to the etching synthesis of Ag NWs (figure 2(c)).

Figures 2(g)–(i) show the growing process of Ag NWs observed in the etching environment. When Ag$^+$ ions were added slowly, PVP repeating units donated lone pairs of electrons to the unoccupied orbital of center Ag$^+$ ions. By the coordination number of 2 (for center Ag$^+$), sp hybridization has to provide two equal orbital in forming comfortable linear coordinating structure. The lone pairs of electrons (on PVP repeating units) take up sp hybridized orbitals of Ag$^+$ for alleviating the electron-deficiency of Ag$^+$ ions and meanwhile, Ag$^+$ ions were reduced to Ag$^0$ by glycolaldehyde (GA) and formed clusters (Ag$^+$, Ag$^2+$, Ag$^3+$ etc) [28, 29]. The presence of PVP can prompt the reduction of Ag$^+$ ions and stabilize corresponding reductive products [30]. Once Ag$^0$ (or clusters) becomes saturated in the solution, the nucleation occurs preferentially in the ligand-rich aggregates, which fixes the uneven ligand distribution. The nanoparticles formed thereby have a wrapped polycentric morphology (figures 2(g) and S4). As the reaction proceeds, due to the thermal fluctuation and induction of Cl$^-$ [14, 23, 31, 32], penta-twined structures were formed in the ligand-rich aggregates. They gradually evolved into Wulff structures and generated new (100) facets, which were subsequently capped by free PVP molecules in the solution, resulting in $\Delta(1000)\to(1111)$ guided axial growth (figures 2(e), (f)) [33]. This process is reflected in figures 2(h), (i), where the NWs bearing root structures can be clearly observed and also verified by further microscope observation (figure S5). Given the wrapped ligand molecules on the surface of polycentric aggregates (figure 2(h)), it is believed that the axial growth of Ag NWs starts from these
wrapped aggregates, which gradually disappear in the process of Ostwald ripening (figure S5(c)). Growth from wrapping morphology indicates that such ligand-rich aggregates are stable, which is the precondition for ‘etching synthesis’.

The etching effect can be observed from the absorbance spectra of the aqueous suspensions at different reaction times. Different morphologies of nanocrystals have different local surface plasma resonances (LSPR), which correspond to different characteristic peaks; for instance, the LSPR peak of Ag nanoparticles is at ~400 nm while for Ag NWs it is around 350–380 nm. A LSPR peak appears at ~400 nm when 3/2 of total Ag⁺ ions were added (corresponding to the reaction time of 15 min), indicating the formation of nanoparticles. When the reaction proceeds to 143 min, a weak shoulder peak appears at ~350 nm (longitudinal LSPR mode), implying the formation of Ag NWs and in accordance with the TEM observation. In this stage, an etching effect was reflected on the decrease in LSPR intensity and a small blue shift when the reaction proceeded to 83 min. This is similar to the typical characteristic of etching process of nanocrystals [21], but has not been observed in the previous Ag NWs-related reports [12]. By removing the nanocrystals produced (figure S6(b)), we determine the rest concentration of Ag⁺⁺⁺ (include Ag⁺, Ag⁰ and their clusters [29]) at different reaction times (C_{real}) by ICP-AES. The conversion rate of Ag⁺⁺⁺ to Ag nanocrystals is calculated according to the equation (1),

\[
\text{Conversion rate} = \frac{(C_{\text{feed}} - C_{\text{real}})V_{\text{real}}}{M_{\text{sum,Ag}}}.
\]

where, for \( t < 23 \text{ min} \), \( C_{\text{feed}} = 50 \times \frac{t+10}{23} \times \frac{107}{169}/V_{\text{real}} \), \( V_{\text{real}} = \frac{t \times 10}{23} + 46 \), and for \( t > 23 \text{ min} \), \( C_{\text{feed}} = 500 \times \frac{107}{169}/V_{\text{real}}, V_{\text{real}} = 56, M_{\text{sum,Ag}} = \text{constant} \).

From figure 3(b), the etching effect can be clearly observed, where a decrease in conversion occurred in the reaction time of 20–143 min. It is noted that the conversions of Ag⁺⁺⁺ at 5, 10 and 143 min are the same (red dash line in figure 3(b)). The decrement at 143 min can be attributed to the nucleation, in view of the obvious LSPR peaks (figure 3(a)); however, indiscernible LSPR peaks at 5 and 10 min should arise from the ligand-rich aggregates. Such a conversion tendency, from increasing to decreasing, indicates that the etching effect is related to the introducing process of AgNO₃, including Ag⁺⁺⁺ and NO₃⁻. To exclude the effect of NO₃⁻, we added the same mole potassium nitrate (KNO₃) as AgNO₃ before introducing AgNO₃. An increased yield (47%) was observed after 3 h. This indicates that the etching effect
primarily originates from Ag\(^+\) itself. Similar observation occurred also in Cl\(^-\). As for Fe\(^{3+}\), a common oxidative etchant, its etching effect is unobvious under N\(_2\) atmosphere for they should be reduced by GA firstly in the synthesis \([34]\). We replace the latter half amount of AgNO\(_3\) with the same mole of ferric nitrate (Fe(NO\(_3\))\(_3\)) at the fixed adding rate. In this case, Ag nanocrystals could be oxidized fully by sufficient Fe\(^{3+}\) from the equation (2).

\[
\text{Fe}^{3+} + \text{Ag}^0 \xrightarrow{\text{oxidize}} \text{Fe}^{2+} + \text{Ag}^+. \tag{2}
\]

However, as shown in figure S7(a), Ag NWs could also be obtained after 3 h with yield of \(\sim 40\%\), but Fe\(^{3+}\) could etch the nuclei formed before addition of Fe(NO\(_3\))\(_3\), which was used to fix the ligand distribution and thereby generated isolated nanoparticles (figure S7(b)).

To further confirm the etching effect of Ag\(^+\) ions, we examined the morphology and yields of products obtained at different adding rates of Ag\(^+\) ions. Two factors affect the etching capability of Ag\(^+\) ions, that is, the concentration of Ag\(^+\) ions and the depleting degree of PVP (the number of free PVP molecules in solution). On the one hand, reducing the adding rate of Ag\(^+\) ions, the number of Ag\(^+\) ions that participate in ligand-rich aggregates decreases, which diminishes the consumption of PVP that forms ligand aggregates. On the other hand, Ag\(^+\) ions have sufficient time to be reduced so

**Figure 2.** The schematic diagram of Ag NW synthesis. Under the reactive condition (N\(_2\), 130 °C), PVP was first dissolved to form a uniform ligand solution (a), to which the Ag\(^+\) (AgNO\(_3\) ethylene glycol solution) solution was added. The Ag\(^+\) ions first added coordinate with PVP, generating some aggregates and diluting the original solution, (b), (c). The nucleation in aggregates is later than PVP capping, resulting in the formation of polycentric wrapped aggregates (d). Ag NWs gradually grow out from the wrapped aggregates (e), (f), (g)–(i) Show TEM images sampled from different reaction times, (g) 83 min, (h) 143 min and (i) 263 min. The inset in (h) shows the complete picture of an aggregate containing one Ag NW.
that the etching effect can be suppressed. Experimentally, when the adding rate of Ag\(^+\) ions was decreased from 100 µl/12.5 s to 100 µl/20 s (that is, a 2-fold decrease), the length of Ag NWs increases 3 times and the yield also increases 3 times, along with a slight increase in the diameter, as shown in figures 4(a), (b), S8–9 and table S1. However, if the AgNO\(_3\) solution was dumped completely (i.e., 100 µl/0 s), Ag\(^+\) ions can coordinate uniformly with the repeating units of PVP, which is not an uneven ligand distribution environment. In this case, more PVP molecules can participate in the stabilization of Ag\(^+\) ions and final products, which weakens the etching effect of Ag\(^+\) and is also unbene\(_f\)icial for the axial growth of NWs [35]. Compared with the conversion of 100 µl/12.5 s, the diameter of 100 µl/0 s increases 1.5 times (figures S8(b), (c)) and the length is almost unchanged, the yield increases to 64% but lower than 76% of 100 µl/20 s. Apparently, these results verify the positive correlation between the etching effect and an uneven ligand distribution. Also, TGA results (figure 4(g)) provide further evidence, which enable us to calculate the molar ratios of the PVP repeating units to surface Ag atoms [27]. As shown in figure 4(h), the corresponding ratios of 100 µl/0 s and 20 s are larger than those of 100 µl/12.5 s and 100 µl/15 s. This is consistent with the etching effect occurred in the synthesis.

3.3. Excellent properties of SG-Ag NWs transparent conductive films (TCFs)

One of important applications of Ag NWs is used to prepare TCFs, the latter has become a promising alternative for expensive ITO films. To prepare high-performance NW films, large aspect ratios and good joint adhesion have been thought to two critical factors that govern the properties of NW films [7, 8, 11]. However, we here demonstrate that reducing the content of high-reactivity defects of Ag NWs could also play an important role in improving the optical, electrical and the use-life of films. To clearly verify this, we took commercial Ag NWs as the control sample, which have an aspect ratio >1000 (HAR-Ag NWs, figure S10) that is 2-fold larger than that of our SG-Ag NWs (∼500). Figure 5(a) shows their XRD curves obtained under the same condition. Compared with SG-Ag NWs, broader diffraction peaks for HAR-Ag NWs implies that they contain more lattice defects, which are in accordance with more wire break sites in figure 1(f) (i.e. more high-reactivity sites).

Through a mild filtration process (figure S11), we prepared TCFs on polyethylene terephthalate (PET) substrate using two kinds of Ag NWs (HAR-Ag NWs and SG-Ag NWs). Their sheet resistances and film transparencies are presented in figure 5(b). Interestingly, although the smaller aspect ratio and larger wire width, compared with HAR-Ag NWs, the SG-Ag NWs film exhibit much lower sheet resistances and much higher transparencies. At the transparency of 93%, the SG-Ag NWs film reveals a sheet resistance of ∼10 Ω/sq. By comparison, the HAR-Ag NWs film shows a value up to ∼80 Ω/sq at the similar transparency. Such excellent properties are apparently related to the few-defect feature of SG-Ag NWs; in other words, a large amount of high-reactivity defects significantly affect the electrical conductivity of HAR-Ag NWs film, although HAR-Ag NWs possess an aspect ratio 2-fold higher than that of SG-Ag NWs.

In addition, the few high-reactivity defects feature of SG-Ag NWs endows the transparent film with excellent air stability. Even after exposing the film in air for 200 days, its sheet resistance did not reveal remarkable variation (figure 6(a), video 1). For HAR-Ag NWs film, it increased almost one order of magnitude within 60 days (figure S12(a)), which agrees with reported works [36, 37, 40]. We also compared the SG-Ag NWs film with the Ag NWs film containing overcoating layers as the previous reports did, and the
results are presented in figure 6(b). The SG-Ag NWs film shows higher transparent conductivity (described by $\sigma_{op}/\sigma_{DC}$, FoM) than those Ag NWs film containing overcoating layers and moreover, even after exposing in air for 200 days, FoM of SG-Ag NW film decreased from 524 to 361, which can still match the highest requirement of applications (FoM $\approx 350$), seeing figure 6(b) red lines.

We believe that the excellent environmental stability of SG-Ag NW films arises from the few high-reactivity defect feature of SG-Ag NWs. In the experiments, it was found that after 200 days’ exposure the color of the EA-Ag NW film changed from white to yellow around the center of the film, with a red edge (see the inset in figure 6(a)). The AFM images reveal that such color variation primarily arises from the oxidative corrosion of SG-Ag NWs. As shown in figures 6(c), (d), many nano-bumps appeared on the surface of NWs after exposure for 120 days and became bigger for 200 days. However, different from the situation that occurred usually in non-etching synthesized NWs, no wire breaks was observed for these SG-Ag NWs. Furthermore, despite slight color variation, the sheet resistance of the SG-Ag NW film increases only from 9.7 to 14.1 $\Omega/\text{sq}$. This is significantly different from the situation occurred in those non-etching synthesized Ag NWs, and further reflected in the variation of the joint state of different kinds of Ag NWs. The joint points between different Ag NWs are highly reactive sites (weak points) that prefer to suffer from oxidative corrosion, due to the ‘hot spot’ effect [5, 43]. The defects can induce structure deformation at the joint point, resulting in the fusion or break of Ag NWs. This is true particularly for those NWs containing high-reactivity defects. As shown in figures S12(b), (c), NWs fusion can be observed in HAR-Ag NWs even after exposure for 120 days.

Figure 4. Morphologies of Ag NWs under different adding rates of Ag$^+$ ions. When the adding rate increases from 100 $\mu$L/20 s to 100 $\mu$L/0 s (the latter implies that the AgNO$_3$ solution was completely dumped), the length of Ag NWs decreases first from $\sim$40 to $\sim$14 $\mu$m, and then increases to $\sim$16 $\mu$m (a)–(c)). The length statistics are shown in (d)–(f) (the data of width and rate of 100 $\mu$L/15 s are also presented in figures S8, S9), the corresponding yields decrease from $\sim$76% to $\sim$28%, then increased to $\sim$64% (table S1). Thermogravimetric analysis (TGA) of Ag NWs under different rates are shown in (g). (h) Gives the molar proportion of loaded PVP units to surface Ag atoms. (The samples used in TGA were washed three times with ethanol, followed by vacuum drying.)
Figure 5. (a) Shows the XRD spectra of SG-Ag NWs and high aspect ratio Ag NW (HAR-Ag NWs). (b) Presents the change in sheet resistance versus transparency, red points for the SG-Ag NW film and black points for the HAR-Ag NWs part. The morphology of HAR-Ag NWs is shown in figure S10.

Figure 6. (a) The electrical conductivities and transparencies of the as-prepared SG-Ag NW films and after exposure in air for 200 days, the inset shows color change of the corresponding films. (b) The comparison between the figure of merits (FoM) versus exposure time in air for our SG-Ag NWs film ($T_{550nm} = 93\%$) and reported results containing coating layers, PPh$_3$ (75%) [36], r-GO/Cu NW (77.6%) [10], PES (89%) [37], TiO$_2$ atomic layer (75%) [38], GO (92%) [9], two-step CVD-graphene (93%) [39], longel (86%) [40], GO-PDDA (91%) [41], CVD-graphene (88%) [3]. Note that all these substrates are PET (except CVD-graphene, quartz) and testing was conducted under room temperature (except r-GO/Cu-Ag NW, 80 °C). FoM expressed by $\sigma_{OP}/\sigma_{DC}$, calculated from $T_{550nm} = \left(1 + \frac{188.5 \sigma_{OP}}{\sigma_{DC}} \right)^{-2}$ [42], where $\sigma_{DC}$ is direct current conductivity, $\sigma_{OP}$ is optical conductivity. (c)–(e) The AFM images directly were obtained from the transparent films on the PET substrate at different exposure times. (c) 0th day, (d) 120th day, (e) 200th day.
placed one day, and break appeared on the 8th day. By comparison, SG-Ag NWs still overlapped on the 200th day and no break or pulverization was observed (figure 6(e)). These experimental observations further indicate the importance of few-defect Ag NWs for high-performance transparent films.

Compared with ITO, another merit of Ag NW films lies in their flexibility, due to the inherent brittle nature of ITO. To demonstrate the flexibility of SG-Ag NW films, we test the bending and stretching capabilities of SG-Ag NW films that were transferred beforehand onto the PET and polydimethylsiloxane (PDMS) substrate, respectively. As shown in figures 7(a), (b), after 1200 bending cycles (bending angle: 90°), the sheet resistance at axle wire (seeing figure 7(a)) only changed from ∼8 to ∼10 ohm/sq, a variation of <30% (seeing figure 7(b)), indicating an excellent bendable character of the SG-Ag NWs film.

After transferred onto the PDMS substrate, a soft, transparent and conductive PDMS film was obtained (figure 7(c)). Using a home-made device (see the inset in figure 7(d)), we also test the stretching property of the SG-Ag NWs film at the strain of 12.5%. As shown in figure 7(d), the percentage of resistance variation after 80 times bending cycles was less than 1 (0.8–1.2 between 0% and 12.5% strain respectively). This strain-sensitive transparent film could control current by fast strain response (video 2). Stretching the film by external force triggers higher resistance and thereby lower current, while the current reset is controlled by the recover degree of stretching strain. Large strain controls low current and high current responds to small strain. It should be noted that although the metal Ag possesses some ductility, the pentagon structure would make Ag NWs more stiffer [15, 44], the flexibility of SG-Ag NWs film should arise from NW networks. We note that the stiffness of SG-Ag NWs networks is slightly higher that of those reported NW networks, see table S2, which might be contributed by few high-reactivity defects character of SG-Ag NWs. Apparently, it is important for Ag NW-based films to achieve
simultaneously expected electrical conductivity, transparency and environmental stability. We expect that this etching synthesis strategy can open a new route for developing high-performance Ag NW-based TCFs.

4. Conclusions

The critical challenge of practical applications for Ag NW films lies in the synergistic improvement in electrical conductivity, transparency, air stability and flexibility. The existing reports have achieved good advances in this regard, however, it remains quite elusive how to achieve such synergistic improvement. The results presented here demonstrate a new, viable concept for performance optimization of Ag NW films. The important finding is that compared with the strategy of increasing aspect ratios of Ag NWs and employing conductive coating layers, reducing the content of high-reactivity defects in Ag NWs seems to be a more effective approach, although they have a low aspect ratio (e.g., 500). We propose a novel etching synthesis method to reduce the high-reactivity defects in Ag NWs. It is found that different from those non-etching synthesized NWs, the etching synthesized, few-defect NWs have a morphology very close to the ideal penta-twined structure and are quite straight. The resulting NW film exhibits an excellent synergistic improvement: the sheet resistance \( \sim 10 \) ohm/sq at optical transparency 93% (550 nm, HF = \( \sim 7\% \)). Even though there were no additional protective coating layers it reveals good air stability: the sheet resistance only increases to 14 ohm/sq after exposed in air for 200 days. In addition, the NW film shows an outstanding flexibility and stretchable capability. We believe that the present work is helpful for addressing the critical issues that retard the practical application of Ag NWs.

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