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Highly flexible, transparent, conductive and antibacterial films made of spin-coated silver nanowires and a protective ZnO layer

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HIGHLIGHTS

- ZnO layer solves the oxidation and adhension problem of AgNWs.
- R_s and transmittance can be controlled by AgNW's deposition number.
- R_s of AgNW/ZnO films remain stable after 1000 bending cycles.
- AgNWs based TCFs show an excellent antibacterial properties.

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ABSTRACT

We prepared highly flexible, transparent, conductive and antibacterial film by spin coating a silver nanowire suspension on a poly (ethylene terephthalate) (PET) substrate. The ZnO layer covered the conductive silver nanowire (AgNW) network to protect the metal nanowires from oxidization and enhance both wire-to-wire adhesion and wire-to-substrate adhesion. It is found that the number of AgNW coatings correlates with both the sheet resistance (R_s) and the transmittance of the AgNW/ZnO composite films. An excellent 92% optical transmittance in the visible range and a surface sheet resistance of only 9 Ω sq^{-1} has been achieved, respectively. Even after bending 1000 times (5 mm bending radius), we found no significant change in the sheet resistance or optical transmittance. The real-time sheet resistance measured as a function of bending radius also remains stable even at the smallest measured bending radius (1 mm). The AgNW/ZnO composite films also show antibacterial effects which could be useful for the fabrication of wearable electronic devices.

1. Introduction

A flexible, highly transparent and conductive film (TCF) could considerably improve the development of flexible electronics, such as flexible OLED displays, flexible optoelectronics and wearable devices [1–4]. The currently most popular transparent conductive material is Indium Tin Oxide (ITO). It is very stable, and it has good conductivity and excellent optical transparency. However, the brittleness of ITO limits its application in flexible electronic devices. Also, the relatively complicated fabrication process of ITO films and the limited supply of Indium further restricts its economic availability in the future [5–8]. Many efforts have been made to develop comparable flexible transparent conductive materials, for example, conductive polymers, carbon nanotubes (CNTs) [9–13], graphene [14–15], metal grids, and random networks of metallic nanowires [16–21]. Silver nanowires with high electrical conductivity (6.3×10^7 S/m) are particularly promising because they approach many optoelectronic properties of ITO [16]. The light scattering properties of silver nanowires improve solar cell efficiency more than other TCFs [22]. Transparent conductive films composed of random AgNW networks can be made relatively easily even on a large scale via solution processing, including spin coating [23], drop casting [16] and rod coating. However, the easily oxidized AgNWs and the weak adhesion between AgNWs and the substrate cause a huge increase in sheet resistance (R_s).

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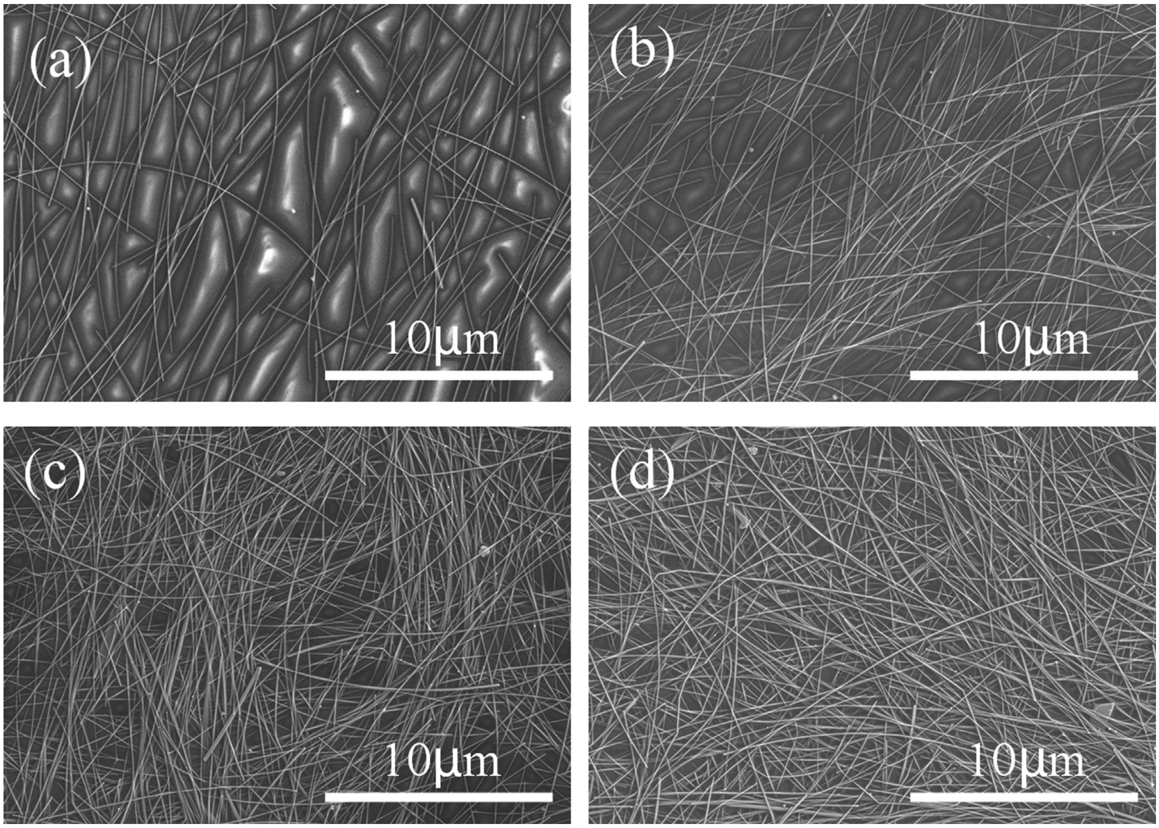

Fig. 1. (a–d) SEM images of the AgNW/ZnO TCFs with the layer deposition numbers 1, 2, 3 and 4 of AgNWs, respectively.

Recently, as an alternative transparent conductive oxide material, ZnO has drawn much attention because of its low cost, nontoxicity, and most importantly: abundance in Earth's crust. However, as flexible transparent electrode material, it has slightly higher resistance than ITO and the same brittleness. We tried to solve the AgNWs' oxidation and adhesion problems by protecting them with another material [24–26]. Conductivity, optical transparency and mechanical bending of the composite films are all largely determined by the density of the AgNWs. The protective layer is the key for enhancing the optical, electrical and mechanical properties of TCFs based on AgNWs. The antibacterial effect is also potentially useful for applications in wearable devices.

In this study, we propose a scalable method to fabricate AgNW/ZnO flexible transparent electrodes on a PET substrate. In order to control the thickness of the protective film, as well as its uniformity, a ZnO precursor film, a few nanometers thick, is used to cover the AgNW network. Their electrical, optical, mechanical and antibacterial properties are studied in detail here. AgNW/ZnO composite TCFs have a big potential to be used in emerging flexible optoelectronic devices like organic light-emitting diodes, liquid-crystal displays, organic solar cells and wearable electronics.

2. Experimental section

2.1. Preparation of the ZnO solution

1 g $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 22.5 mL of ethanol and then the solution was stirred well at 40 °C for 2 h. Subsequently, lactic acid diluted with deionized water was added to the solution, drop by drop, until the solution became completely colorless and transparent. The solution was kept at 65 °C for 2 h and then cooled down to room temperature. The ZnO solution was then resting for 2 days in order to increase its viscosity before it was used.

2.2. Fabrication of AgNW/ZnO composite films

AgNWs were synthesized via a solution-phase method [27]. Before use, AgNWs were dispersed in isopropyl alcohol with a concentration of 3 mg/ml. The average diameter and length of AgNWs were 40 nm and 35 μm, respectively. The AgNW suspension was deposited on poly (ethylene terephthalate) (PET) substrates by spin coating at 3000 rpm. After the coating, the films were dried at 90 °C for 10 min. The procedure was repeated to create AgNW network of different densities. The ZnO precursor solution was coated on top of the AgNW films to act as a protective layer. Subsequently, the films were dried at 65 °C for 10 min followed by a heat treatment at 180 °C for 20 min.

2.3. Antibacterial assay

The *Escherichia coli* (ATCC25922, American Type Culture Collection) was cultured in a Mueller–Hinton (MH) Broth. Prior to assays, the cells were grown overnight to a stationary phase, at 37 °C in a 5 ml MH Broth. After incubation, 100 μL of bacteria was suspended in a 5 ml of fresh MH Broth for an additional hour at 37 °C to obtain a mid-log-phase culture. The logarithmic cultures were diluted to an inoculum size of 106 CFU (colony forming unit) in a fresh Mueller–Hinton Broth medium and drop coated on the transparent conductive films and finally incubated overnight at 37 °C. The cells were then taken and serially diluted after treatment and plated on Mueller–Hinton agar plates of 7 cm diameter for CFU counting.

2.4. Characterization

The morphology of the AgNW/ZnO composite films was

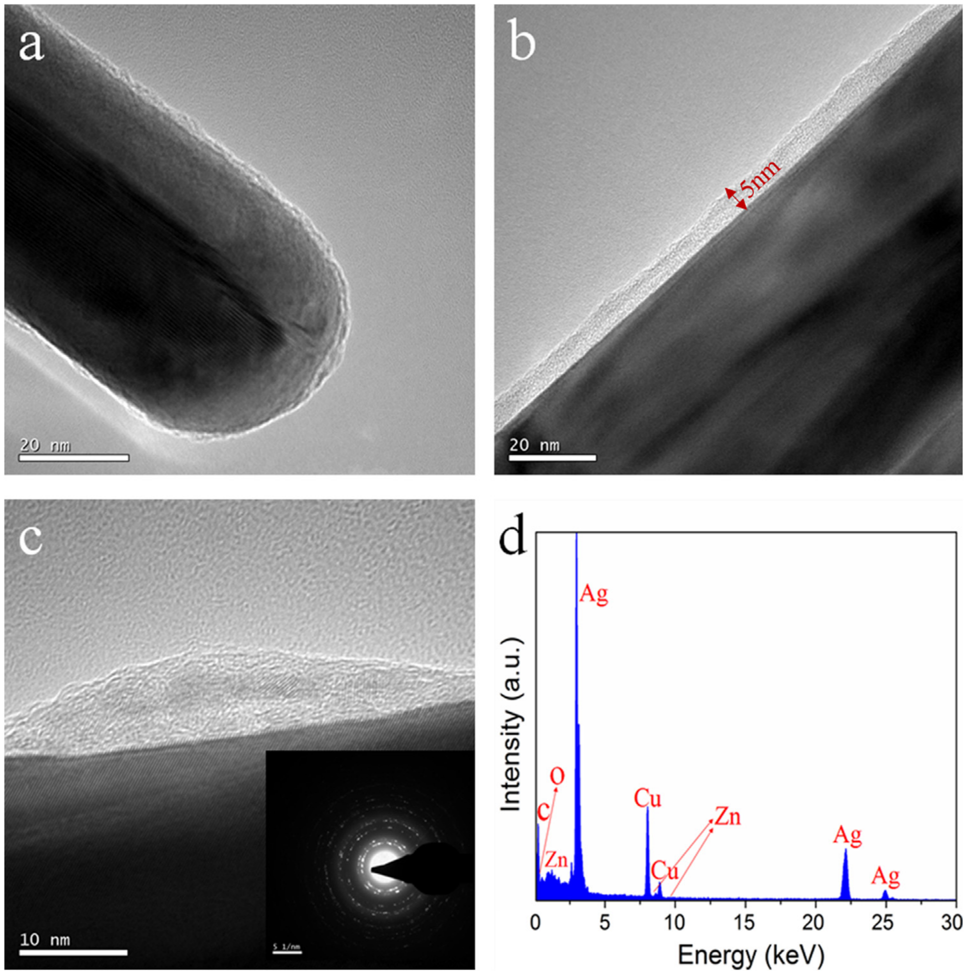

Fig. 2. (a–c) TEM images of AgNW/ZnO TCF; (c) the inset shows the SAED pattern; (d) EDX analysis of the composite film.

observed by field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F30). The sheet resistance was measured using the standard four-point probe technique. The optical transmission spectrum was measured using a double-beam spectrophotometer (SHIMADZU, UV-3101) with air as reference. The bending test was carried out with a self-made bending device.

3. Results and discussion

The flexible AgNW/ZnO composite film was prepared on a PET substrate via spin coating the ZnO precursor on the AgNW network. Both conductivity and transmittance of the composite AgNW/ZnO film depend on the density of the AgNWs. When the concentration of the AgNW suspension and the rotation speed of spin coating are given, the AgNW density can be controlled by adjusting the number of spin coating layers. This way, both the sheet resistance (R_s) and optical transmittance of the composite film can be determined. A high number of layers produces denser TCFs. Fig. 1a–d shows SEM images of the AgNW/ZnO TCFs for different layer numbers (coating cycles) of AgNWs. It shows that the AgNWs have formed a conductive network already after the first coating cycle (Fig. 1a). Therefore the TCF has the ability to conduct electrons quite well. The more coating cycles are used, the denser the AgNW TCF (Fig. 1a–d) became. A denser AgNW TCF is expected to have both lower R_s (more paths to conduct electrons are available) and lower light transmittance. As a consequence, to meet different application requirements, different flexible AgNW/ZnO TCFs can be fabricated by simply adjusting the number of spin coating cycles of the AgNWs.

To check the uniformity of the ZnO film on AgNWs, typical TEM images of the AgNW/ZnO composite films are shown in Fig. 2a–b. The AgNWs appear to be covered by an about 5 nm thick protective layer. Energy dispersive X-ray spectroscopy (EDS) analysis is shown in Fig. 2d, which confirms the covered layer is Zn–O. The selected area electron diffraction (SEAD) image in Fig. 2c (inset) indicates that the protective ZnO layer has not crystallized completely, probably because of the low annealing temperature. After the AgNW network had been formed, the ZnO precursor protective layer was deposited. Therefore it is not expected that the protective layer will have a negative effect on the junction resistance between the AgNWs.

To obtain a transparent conductive film, the films should have high optical transparency for visible light and high electrical conductivity. Fig. 3 shows the optical transmittance and R_s measurement of both AgNW TCFs and AgNW/ZnO TCFs as a function of the number of AgNW spin-coating cycles. As shown in Fig. 3a, it can be found that the ZnO layer has only a small effect on the optical transmittance. All of the AgNW/ZnO composite TCFs are transparent so that our University logo is clearly visible through the TCFs (Fig. 3c). Clearly, the optical transmittance decreases for higher numbers of AgNW deposition cycles. This is due to the higher AgNW density produced by multiple coatings as well as the diffuse light scattering properties of AgNWs. Light scattering is very beneficial to the photon collection efficiency if used in solar

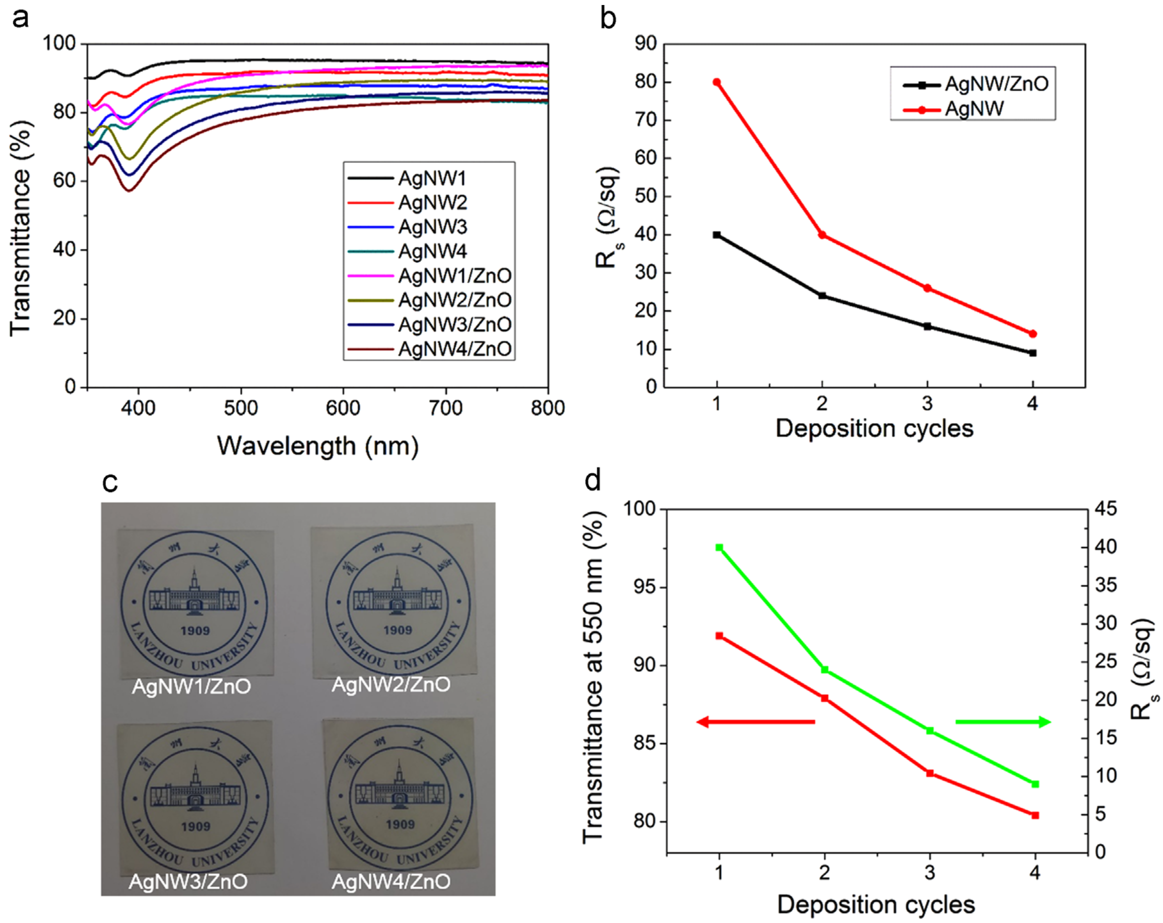

Fig. 3. (a) Transmittance and (b) R_s of the AgNW based TCFs deposited at different deposition cycles; (c) photographs showing the AgNW/ZnO composite TCFs after different deposition cycle numbers; (d) transmittance at the wavelength of 550 nm and R_s of the AgNW/ZnO TCFs as a function of AgNW deposition cycles.

cells [22]. As seen from the Fig. 3b, it is noteworthy that the R_s of the AgNW/ZnO TCFs is on average about 41% smaller than the one of the AgNW TCFs. In the annealing process, the ZnO protective layer tightened the contacts between AgNWs, thereby reducing the junction resistance between the individual AgNWs. The melting point of silver nanomaterials is very low, which helps to trigger self-welding between AgNWs during the annealing process. The above depicted factors lead to the overall decrease of the internal resistance of AgNW/ZnO TCFs. As the number of AgNW deposition cycles increases from one to two, three, and four, the optical transmittance values of AgNW/ZnO composite TCFs at the wavelength of 550 nm decrease from 92.0% to 87.9%, 83.1%, and 80.4% and the sheet resistance decreases from 40 Ω/sq to 24 Ω/sq, 16 Ω/sq, 9 Ω/sq, respectively. In other words, the optical transmittance at 550 nm and the R_s of the AgNW/ZnO TCFs follow a near linear relationship with the number of AgNW deposition cycles (Fig. 3d).

Due to their excellent bending property, the metallic nanowire network has a great potential to serve as a flexible electrode in many devices. As a promising alternative to conventional ITO, the transparent conductive AgNW/ZnO composite films should have better flexibility and are less likely to crack. The bending test was carried out on the AgNW/ZnO composite film with a self-made bending device. The films were bent at the bending radius of 5 mm at a frequency of 30 min^{-1}. The R_s change ratio of AgNW/ZnO TCFs on PET substrate were measured after bending a given number of cycles. Fig. 4a shows the mechanical flexibility of the AgNW/ZnO, AgNW and ITO TCFs as a function of bending cycles. It can be seen, even after 1000 bending cycles, the R_s of the AgNW/ZnO composite TCFs nearly stays the same. The R_s of AgNW TCFs changes from 22 Ω/sq to 42 Ω/sq after 600 bending cycles. After 1000 bending cycles, the R_s of the AgNW TCFs rapidly increases to about 10 times its original value (from 22 Ω/sq to 218 Ω/sq). We believe this is due to the unfavorable interconnection among AgNWs and poor adhesion between AgNWs and PET substrate. The R_s of the ITO film becomes about 7 times larger (from 36 Ω/sq to 253 Ω/sq) than its initial R_s (Fig. 4a) because of its brittleness. Overall, the flexibility related properties of AgNW TCFs are still worse than those of the ITO TCFs on PET substrates, but they have been significantly improved by protecting the AgNW network TCFs with ZnO films.

We then measured the real-time changes of R_s as a function of bending radius (Fig. 4b inset). Fig. 4b shows the R_s change ratio of the AgNW, AgNW/ZnO and an ITO TCFs as a function of bending radius. Clearly, the AgNW/ZnO TCFs and the AgNW TCFs show a smaller sheet resistance change than the ITO film. When the bending radius is 1 mm, the R_s of the AgNW/ZnO composite films increases to 36.8 Ω/sq, and the AgNW film increases to 38 Ω/sq. However, the sheet resistance of the ITO films reaches 3.4 kΩ/sq when the bending radius is only 5 mm, and further increases to 17 kΩ/sq when the bending radius is 4 mm. This confirms the mechanical flexibility of the AgNW-based TCFs is superior to ITO, especially the one of AgNW/ZnO TCFs due to the outstanding flexibility of the AgNWs. The R_s change of AgNW/ZnO composite TCFs with and without 1000 bending cycles as a function of bending radius (Fig. 4c) was also compared. The R_s of the two samples nearly stays the same when the bending radius is more than 2 mm. This indicates that the 1000 bending cycles affect the

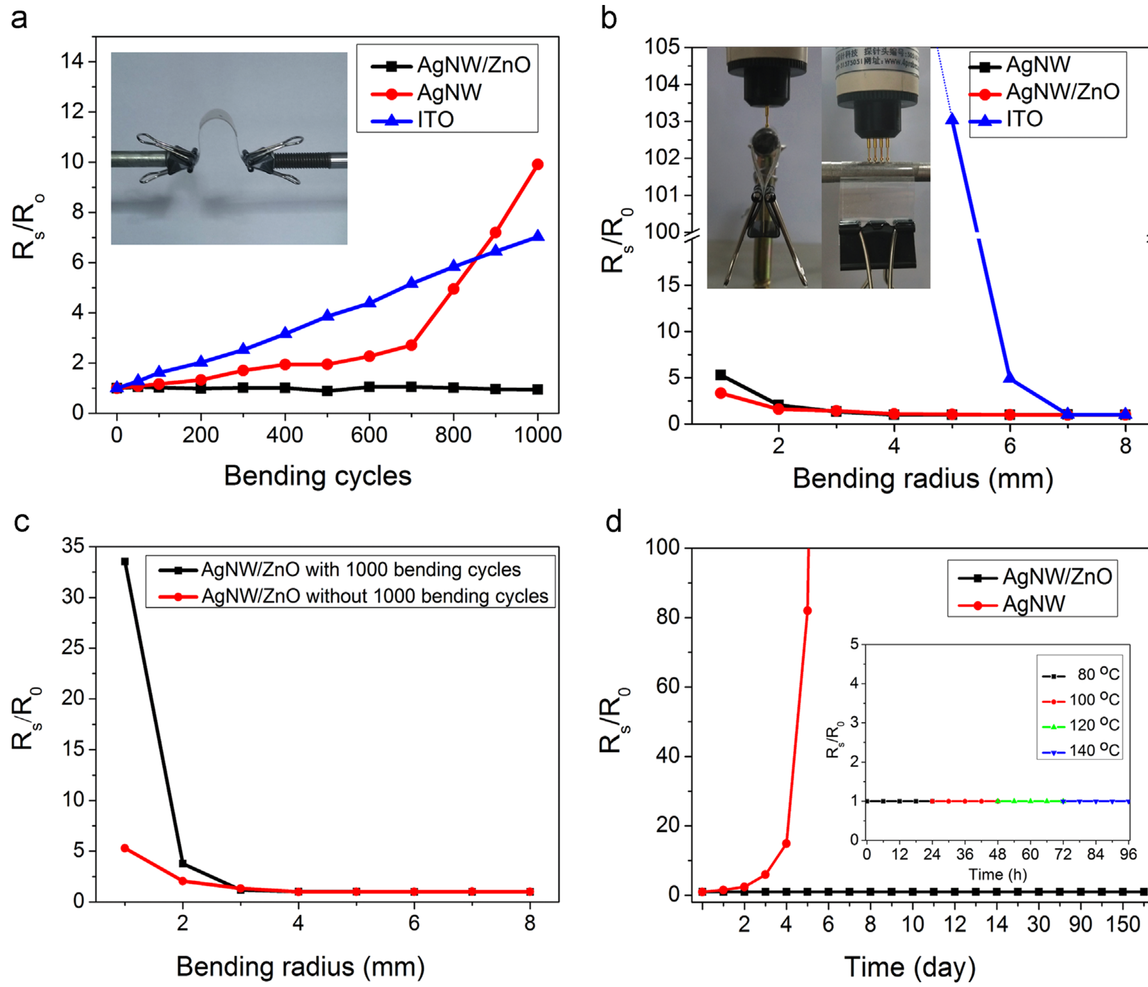

Fig. 4. R_s change ratio of ITO, AgNW and AgNW/ZnO TCFs as a function of bending cycles (a) and bending radius (b); (c) R_s change ratio of AgNW/ZnO TCFs with and without 1000 bending cycles as a function of bending radius; (d) R_s change ratio of the AgNW based TCFs exposed to 80 °C air.

AgNW/ZnO composite TCF very little. Therefore, it can be concluded that the AgNW/ZnO composite TCFs have better mechanical flexibility than both AgNW TCFs and the ITO TCFs. We attribute this improvement to the ZnO protection layer as it probably enhanced the adhesion performance of wire-to-wire as well as wire-to-substrate.

In order to test the long-term stability of the AgNW based TCFs, the AgNW/ZnO and the AgNW TCFs were kept at 80 °C for half a year. The R_s of the AgNW/ZnO composite TCFs remains nearly the same. However, the R_s of the AgNW TCFs increases to ~15 kΩ/sq after 7 days (Fig. 4d). In addition, the AgNW/ZnO TCFs was kept at 80 °C, 100 °C, 120 °C and 140 °C for 24 h, respectively. The R_s of the AgNW/ZnO TCFs still stays the same (Fig. 4d inset). This suggests that the ZnO layer can successfully protect the AgNWs from oxidation and maintain their high electrical conductivity. Another important advantage of AgNW covered by the ZnO layer is the excellent mechanical protection from adhesion, friction, and negative bending effects.

To further check the mechanical stability and the adhesion between the AgNWs and the PET substrate, a Sello-tape test was carried out on the AgNW films and AgNW/ZnO composite films. The sheet resistance was measured before and after the test. The AgNW films with 44 Ω/sq R_s became non-conductive after just one Sello-tape test. This is probably because the AgNW network was completely removed by the Sello-tape. However, the R_s of the AgNW/ZnO composite film remains almost unaffected with sheet resistances staying between 15.6 Ω/sq and 17.3 Ω/sq even after the test was performed 10 times. Therefore, the protecting ZnO layer plays an important part by enhancing the wire-to-wire and wire-to-substrate adhesion i.e. the mechanical stability of the AgNW TCFs.

When transparent conductive films are used in certain specialized applications, such as wearable devices, an antibacterial effect would be beneficial. Because of the presence of Ag, an antibacterial effect is expected to occur in the AgNW based TCFs. To test this, a diluted bacterial solution was drop-coated on PET, AgNW and AgNW/ZnO TCFs and incubated overnight. The digital photograph of three samples after this treatment can be seen in Fig. 5a–c. As seen in Fig. 5a, the blank PET substrate shows a big white dot indicating no antibacterial effect. In contrast to the blank PET substrate, the two AgNW based TCFs show antibacterial effects (Fig. 5b and c). The number of bacterial colonies on two AgNW based TCFs was much smaller than on the blank PET substrate (Fig. 5d). The antibacterial effect of the AgNW/ZnO composite films and the AgNW films may be attributed mainly to the AgNWs which are capable to release silver ions to inhibit bacterial growth [28]. After being covered by the thin ZnO protection layer, some silver ions could have been released from AgNWs and passed through the thin ZnO layer to cause the antibacterial effect. Further studies may likely improve and clarify the antibacterial properties of AgNW/ZnO composite films.

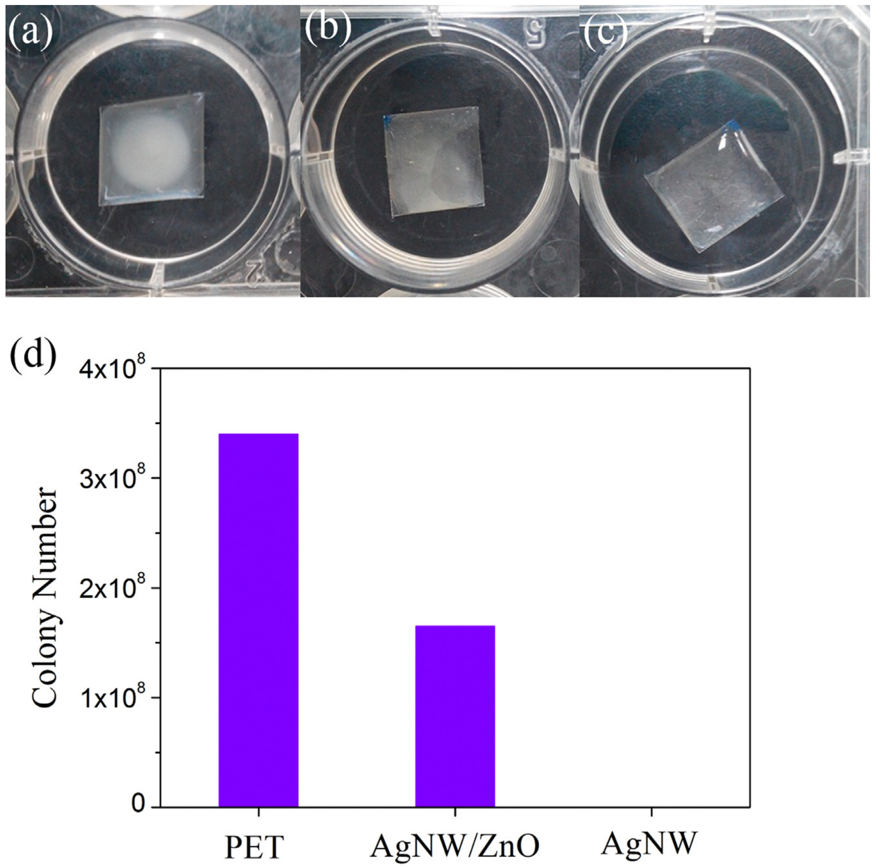

Fig. 5. (a–c) The photograph of PET, AgNW/ZnO and AgNW TCFs after one night incubated in an incubator; (d) Histogram of the colony number of each film.

4. Conclusions

We have presented a simple method to prepare a highly flexible AgNW/ZnO composite TCF with antibacterial effect. The sheet resistance and optical transmittance of the films can be controlled by adjusting the number of AgNW layers (spin coating cycles) as well as the concentration of the AgNW dispersion. The transparent conductive AgNW/ZnO composite films show excellent mechanical flexibility and long-term stability. The AgNW/ZnO composite TCFs remain conductive even after bending (1 mm bending radius) and ten Sello-tape tests. In summary, our results indicate that the AgNW/ZnO TCF composites have a great potential to improve flexible electronics including organic light-emitting diodes, liquid-crystal displays, organic solar cells and wearable electronic devices.

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References

[1] D. Angmo, F.C. Krebs, Flexible ITO-free polymer solar cells, J. Appl. Polym. Sci. 129 (1) (2013) 1–14.
[2] C.H. Liu, X. Yu, Silver nanowire-based transparent, flexible, and conductive thin film, Nanoscale Res. Lett. 6 (2011) 75–83.
[3] X.Y. Zeng, Q.K. Zhang, R.M. Yu, C.Z. Lu, A new transparent conductor: silver nanowire film buried at the surface of a transparent polymer, Adv. Mater. 22 (2010) 4484–4488.
[4] J.W. Lim, D.Y. Cho, K. Eun, S.H. Choa, S.I. Na, J. Kim, H.K. Kim, Mechanical integrity of flexible Ag nanowire network electrodes coated on colorless PI substrates for flexible organic solar cells, Sol. Energy Mater. Sol. Cells 105 (2012) 69–76.
[5] C.J.M. Emmott, A. Urbina, J. Nelson, Environmental and economic assessment of ITO-free electrodes for organic solar cells, Sol. Energy Mater. Sol. Cells 97 (2012) 14–21.
[6] C.H. Chung, T.B. Song, B. Bob, R. Zhu, Y. Yang, Solution-processed flexible transparent conductors composed of silver nanowire networks embedded in indium tin oxide nanoparticle matrices, Nano Res. 5 (2012) 805–814.
[7] B. Azzopardi, C.J.M. Emmott, A. Urbina, F.C. Krebs, J. Mutale, J. Nelson, Economic assessment of solar electricity production from organic-based photovoltaic modules in a domestic environment, Energy Environ. Sci. 4 (2011) 3741–3753.
[8] F.C. Krebs, T. Tromholt, M. Jørgensen, Upscaling of polymer solar cell fabrication using full roll-to-roll processing, Nanoscale 2 (2010) 873–886.
[9] D.S. Hecht, L.B. Hu, G. Irvin, Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures, Adv. Mater. 23 (2011) 1482–1513.
[10] Z.C. Wu, et al., Transparent, conductive carbon nanotube films, Science 305 (2004) 1273–1276.
[11] L. Hu, D.S. Hecht, G. Gruner, Percolation in transparent and conducting carbon nanotube networks, Nano Lett. 4 (2004) 2513–2517.
[12] M. Zhang, et al., Strong, transparent, multifunctional, carbon nanotube sheets, Science 309 (2005) 1215–1219.
[13] M.W. Rowell, et al., Organic solar cells with carbon nanotube network electrodes, Appl. Phys. Lett. 88 (23) (2006) 233506.
[14] S. Bae, et al., Roll-to-roll production of 30-inch graphene films for transparent electrodes, Nat. Nanotechnol. 5 (2010) 574–578.
[15] K.S. Kim, et al., Large-scale pattern growth of graphene films for stretchable transparent electrodes, Nature 457 (2009) 706–710.
[16] J.Y. Lee, S.T. Connor, Y. Cui, P. Peumans, Solution-processed metal nanowire mesh transparent electrodes, Nano Lett. 8 (2008) 689–692.
[17] H. Wu, et al., Electrospun metal nanofiber webs as high-performance transparent electrode, Nano Lett. 10 (2010) 4242–4248.
[18] P.C. Hsu, et al., Passivation coating on electrospun copper nanofibers for stable

transparent electrodes, ACS Nano 6 (2012) 5150–5156.
[19] L.B. Hu, H. Wu, Y. Cui, Metal nanogrids, nanowires, and nanofibers for transparent electrodes, MRS Bull. 36 (2011) 760–765.
[20] A.R. Rathmell, S.M. Bergin, Y.L. Hua, Z.Y. Li, B.J. Wiley, The growth mechanism of copper nanowires and their properties in flexible, transparent conducting films, Adv. Mater. 22 (2010) 3558–3563.
[21] A.R. Rathmell, B.J. Wiley, The synthesis and coating of long, thin copper nanowires to make flexible, transparent conducting films on plastic substrates, Adv. Mater. 23 (2011) 4798–4803.
[22] H.A. Atwater, A. Polman, Plasmonics for improved photovoltaic devices, Nat. Mater. 9 (2010) 205–213.
[23] D.S. Leem, A. Edwards, M. Faist, J. Nelson, D.D.C. Bradley, J.C. Mello, Efficient organic solar cells with solution-processed silver nanowire electrodes, Adv. Mater. 23 (2011) 4371–4375.
[24] D.R. Sahu, S.Y. Lin, J.L. Huang, ZnO/Ag/ZnO multilayer films for the application of a very low resistance transparent electrode, Appl. Surf. Sci. 252 (2006) 7509–7514.
[25] K.S. Kao, S.H. Chang, P.T. Hsieh, C.M. Wang, D.L. Cheng, Transparence and electrical properties of ZnO-based multilayer electrode, Appl. Phys. A – Mater. Sci. Process. 96 (2009) 529–533.
[26] D.R. Sahu, J.L. Huang, High quality transparent conductive ZnO/Ag/ZnO multilayer films deposited at room temperature, Thin Solid Films 515 (2006) 876–879.
[27] B. Wiley, Y. Sun, B. Mayers, Y. Xia, Shape-controlled synthesis of metal nanostructures: the case of silver, Chem. Eur. J. 11 (2005) 454–463.
[28] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, et al., A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*, J. Biomed. Mater. Res. 52 (2000) 662–668.