J Mater Sci (2023) 58:17816–17828

Electronic materials

Stability enhancement and patterning of silver nanowire networks by conformal TiO_2 coating for flexible transparent conductive electrodes

Yalian Weng[1,*], Guixiong Chen[2], Xiongtu Zhou[2,3,*], Yongai Zhang[2,3], Qun Yan[2,3], and Tailiang Guo[2,3]

[1] Xiamen Key Laboratory of Optoelectronic Materials and Advanced Manufacturing, Institute of Luminescent Materials and Information Displays, College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, People's Republic of China

[2] College of Physics and Information Engineering, Fuzhou University, Fuzhou 350108, Fujian, People's Republic of China

[3] Fujian Science and Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350108, Fujian, People's Republic of China

Received: 30 August 2023
Accepted: 11 November 2023
Published online:
5 December 2023

ABSTRACT

Highly stable and patterned silver nanowire (AgNW) networks are essential and challenging for flexible or wearable electronics. In this work, TiO_2 coatings by atomic layer deposition (ALD) technique were introduced for the fabrication of highly stable and patterned AgNW/TiO_2 composites for flexible transparent conductive electrodes (TCEs). It was found that TiO_2 coating could not only enhance the adhesion of AgNWs to the substrate, but also improve the flexibility of AgNW networks. This phenomenon was owed to the stability enhancement by the three-dimensional conformal deposition of TiO_2 coatings. What's more, the thermal and oxidation stabilities of AgNW networks could be greatly improved because of the barrier performance of TiO_2 coating layer. Based on the stability enhancement by TiO_2 coatings, a novelty patterning method of the AgNW networks was implemented by cooperating with photolithography and ultrasonic concussion process. AgNW networks with the strip width of 200 μm were well patterned without defects. Finally, highly stable and patterned AgNW/TiO_2 composites were applied as flexible TCEs for alternating current electroluminescent (ACEL) devices. The whole ACEL device showed a high transparency of around 40%, and the flexibility and the lifetime of ACEL devices were correspondingly improved owe to the enhancement by TiO_2 coatings. These results indicated the prospects of the AgNW/TiO_2 composites on the applications to flexible or wearable electronics.

Handling Editor: Maude Jimenez.

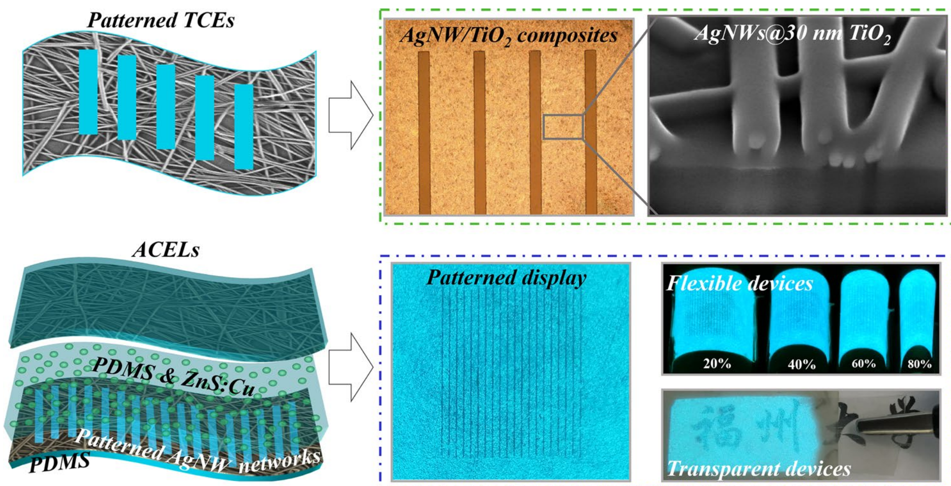
Yalian Weng and Guixiong Chen have equally contributed to this work.

Address correspondence to E-mail: ylweng@hqu.edu.cn; xtzhou@fzu.edu.cn

https://doi.org/10.1007/s10853-023-09152-5

GRAPHICAL ABSTRACT

TiO_2 coatings by atomic layer deposition (ALD) technique were introduced for the fabrication of highly stable and patterned AgNW/TiO_2 composites for flexible transparent conductive electrodes (TCEs).



Introduction

Transparent conductive electrode (TCE) is a critical component within a wide range of electronic and optoelectronic devices. To date, wide bandgap conductive metal oxides such as indium tin oxide (ITO) and Al-doped zinc oxide (AZO), have been the most successfully commercialized transparent conductive material. On the other hand, with the fast development of flexible and wearable electronics, flexible TCEs are highly desired and have been extensive researched in the past decades [1–5]. However, challenges still remain to be solved urgently for the flexible or stretchable TCEs, if the electronic devices would be integrated on wearable devices or freely attached on human skin without any discomfort [6–8]. During the past decades, many kinds of nanomaterials have been studied for the fabrication of flexible TCEs, such as graphene-based electrodes, metallic nanowires electrodes, conductive polymers and dielectric-metal-dielectric (DMD) electrodes. Most of the above nanomaterials possess good physical properties, while the vital drawbacks like high price, potential scarcity or brittleness, limited their commercialization [9, 10]. Silver nanowires (AgNWs) attracted great attention because of its excellent physical performances. AgNW is a kind of one-dimensional nanomaterial with high aspect ratio, which make it easy to establish planar conductive film than metallic particles or flakes. Besides, the AgNW networks show extremely higher electrical conductivity and excellent deformation properties, which were expected to be a good candidate for flexible TCEs [11–13].

In order to further realize the industrial application of AgNWs for flexible TCEs, the research community has committed to enhance the stability of AgNW networks. Many studies have shown that silver was easily oxidized or degraded when exposed to air, acid or sulfur-containing environment. Therefore, the flexible TCEs based on the AgNWs will be unstable if it works under severe conditions for a long time [14]. In addition, AgNWs tend to be spheroidized when subjected to high temperature, which will greatly affect the conductivity of the AgNW networks. This unstable phenomenon is also called Plateau–Rayleigh instability [15]. All these factors are the main problems when integrating AgNW networks into optoelectronic devices. It was reported that AgNW nanocomposites covering another capping material on the surface of the AgNW networks could improve the instability of the AgNWs. The capping materials commonly include nanoparticles, carbon-based conductive materials, polymers or metal oxides, etc [16–20]. The nanocomposite conductive structure of AgNW networks mainly has two purposes: one is to reduce the potential instability of AgNWs, and the other is to combine complementary materials to improve the comprehensive properties. Among the capping materials, metal oxides have been widely studied to modified the AgNW networks in recent years, exhibiting significant stability enhancements without reducing the optical transparency [21–24]. For example, Aghazadehchors et al. confirmed that the bilayer coatings of 70 nm ZnO/70 nm Al_2O_3 could enhance the thermostability of AgNW networks [25]. Song et al. covered a sol–gel coating of titanium dioxide (TiO_2) on the surface of AgNWs to improve the thermal and chemical stabilities of AgNWs [26]. Furthermore, the metal oxide coatings can also enhance the adhesion of the AgNWs to the substrate and improve the stability and service life of overall structure by introducing surface modifiers to strengthen the chemical binding between AgNWs and metal oxide coatings [27, 28].

TiO_2 film is a cheap semiconductor with superior optical and electrical properties, such as high surface area, excellent thermal and chemical stabilities, moderate electron transfer ability and wide band gap energy, and new processes have been developed to explore the potential application of TiO_2 on AgNWs electrode modification and make it more widely used [29–32]. To superimpose the performance of the coating layer and the AgNWs, the TiO_2 coating layer should be able to improve the bending performance of the AgNWs/TiO_2 composites as far as possible without affecting the transmittance and working stability [26]. TiO_2 film can be normally fabricated by the conventional methods of e-beam evaporation, sol–gel processing, sputtering, scratching, and rod coating. However, in view of the homogeneity, conformality and thickness controllability of the films, atomic layer deposition (ALD), a special CVD technique with excellent three-dimensional conformality, large-area uniformity, precise sub-monolayer film thickness control and low-temperature growth, is considered as the promising technique to deposited the TiO_2 coating layer for AgNW networks to make it withstand a certain degree of bending and stretching [33–36].

In this work, we studied the modification of AgNW networks by TiO_2 coating using ALD to obtain highly stable patterned flexible TCEs. Optical transmittance, electrical conductivity, mechanical properties and working stability of the flexible TCEs were investigated to determine the effects of TiO_2 coatings on the AgNW networks. In addition, a novel patterning technique of AgNW networks was developed by using photolithography and ultrasonic concussion process. At last, the patterned flexible TCEs were applied to alternating current electroluminescent (ACEL) devices for further verification.

Experimental methods

Fabrication of AgNW networks

AgNWs ink was purchased from COLDSTONES TECH (CST-NW-S30). The average diameter and length of AgNWs were 30 ± 3 nm and 25 ± 5 μm, respectively. The solvent of AgNWs ink was isopropyl alcohol and the concentration of AgNWs was 10 mg/ml. Poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) was used as substrate for AgNW networks, which prepared by mixing the base polymer with crossing-linking agent in a ratio of 10:1 and then spin-coated on glass substrates. The coated PDMS was cured at the temperature of 90 ℃ for 90 min to form solidified PDMS films with an average thickness of 300 ± 5 μm. Before spin-coating, the substrates were ultrasonic cleaned with detergent solution, acetone and deionized water for 15 min, respectively. Subsequently, the substrates were treated by oxygen plasma treatment for 5–10 min. Then, AgNWs ink was spin-coated on the substrate, and then passed for annealing at 130℃ for 15 min in the air to remove the solvent and welded the cross nodes between AgNWs to form a AgNW networks.

Deposition of TiO_2 coating by ALD

The atomic layer deposition (ALD, BENEQ TFS-200) system was applied to deposit conformal TiO_2 coating layers on AgNW networks. The temperature of the reaction chamber was kept at a low temperature of 90 ℃. Titanium tetrachloride ($TiCl_4$) and water (H_2O) were two precursors for the fabrication of TiO_2 thin films. The carrier gas of precursors was high purity N_2 (99.999%) with flow rate of 20 sccm. A reaction cycle of TiO_2 contained the following pulses: $TiCl_4$ pulse for 0.3 s, N_2 purging for 2 s, H_2O pulse for 0.3 s and N_2 purging for 2 s. Thus, the ALD sequences were repeated to obtain the desired thicknesses. Different thicknesses of TiO_2 thin films were investigated as the coating layers for AgNW networks.

Patterning of AgNW networks

AgNW networks with conformal coated TiO_2 were patterned by a new developed photolithographic process by cooperating with ultrasonic concussion, as shown in Fig. 1. Briefly, AgNWs were firstly spinning coated on PDMS substrate to form a AgNW networks (step 1). Then, positive photoresist (PR, RZJ-304) was uniformly spin-coated on the AgNW network at 2000 rpm for 30 s, and was passed for annealing at 100 ℃ for 2 min (step 2). Next, the AgNW networks capped with PR layer were exposed to UV light for 20 s with a patterned photo-mask (step 3). The graphics of PR layer was developed by using positive developer (RZX-3038) for 30 s, followed by the rinse with deionized water, and annealing at 120 ℃ for 2 min (step 4). After that, the samples were transferred to ALD system to for the deposition of 30 nm TiO_2 coating layers (step 5). The samples were then immersed in isopropyl alcohol solution, followed with ultrasonic concussion in a ultrasonic cleaner (Skymen, JTS-1030, power = 500 W) for 30 min to remove the PR together with the underneath AgNWs, while the AgNWs with TiO_2 coatings remained due to the enhanced adhesion (step 6). Finally, the samples were purged by high purity N_2 (99.999%) to remove the residual impurity and solution, and the patterned AgNW networks were successfully fabricated (step 7).

Results and discussion

TiO_2 coating on AgNW networks by ALD

TiO_2 films were deposited on the surface of AgNW networks to improve the stability. The surface morphology of the AgNW networks and the TiO_2 coating state were observed by SEM. As shown in Fig. 2a and Figure S1(a), the AgNWs were randomly and uniformly distributed on the surface of the PDMS substrate after spin-coating and thermal annealing at 130 ℃ for 15 min. And the junctions between the AgNWs were then welded after thermal annealing, which could not only greatly improve the conductivity of the AgNW networks, but also enhanced the mechanical stability to a certain degree [37]. The effects of TiO_2 coating layer by ALD with different thicknesses on the performance of AgNWs/TiO_2 composites for flexible TCEs were further investigated. For clarity, the AgNW networks with 30 nm (50 nm or 80 nm) TiO_2 coating were denoted as AgNWs@30 (50 or 80) nm TiO_2, respectively. Figure 2b–d and Figure S1(b–d) show the SEM images for TCEs of AgNWs@30 nm TiO_2, AgNWs@50 nm TiO_2 and AgNWs@80 nm TiO_2, respectively. It can be clearly seen that conformal TiO_2 thin films with different deposition thicknesses were

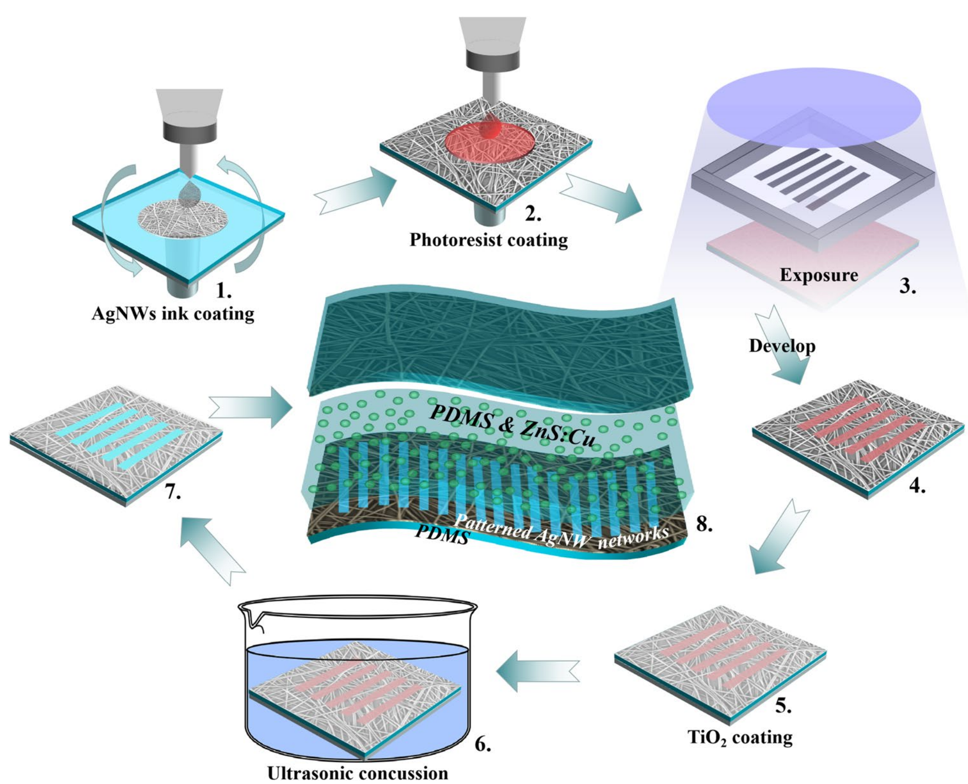


Figure 1 Schematic illustration for the fabrication of patterned flexible TCEs for ACEL devices.

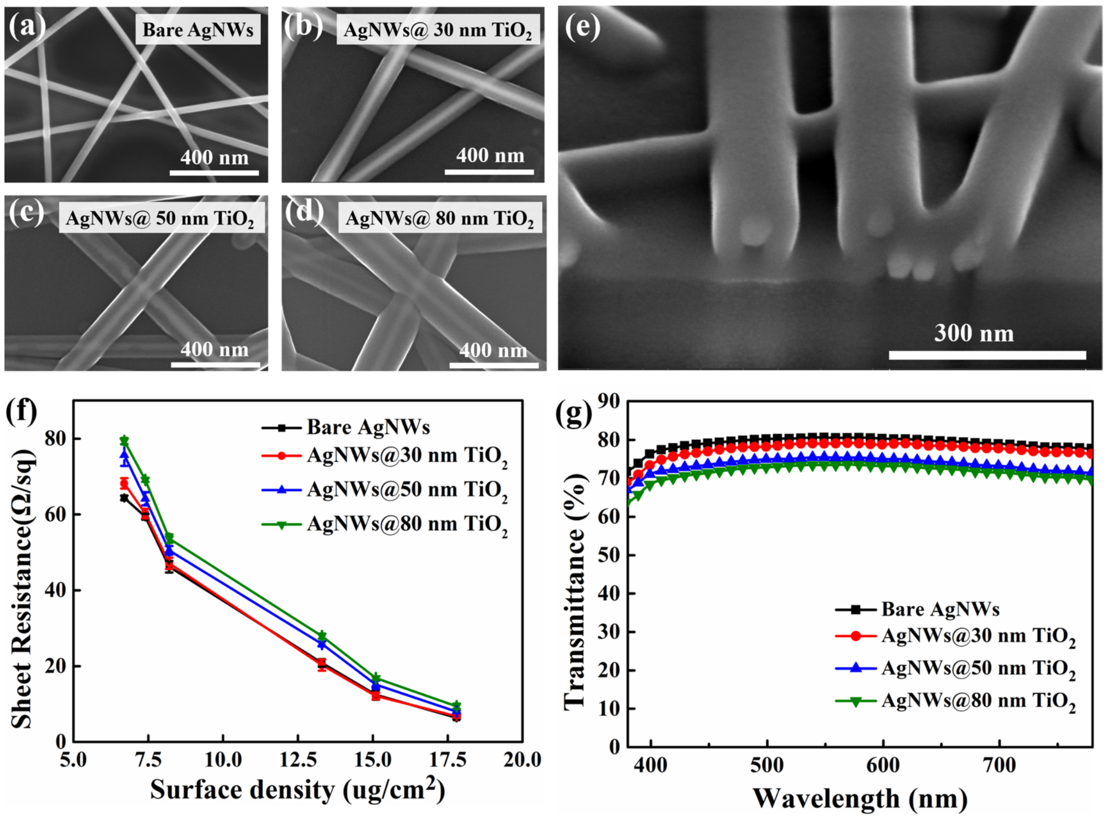


Figure 2 SEM images of AgNWs/TiO_2 composites for flexible TCEs: **a** bare AgNWs, **b** AgNWs@30 nm TiO_2, **c** AgNWs@50 nm TiO_2 and **d** AgNWs@80 nm TiO_2. **e** The cross sectional image of AgNWs@30 nm TiO_2. **f** Sheet resistances of AgNW networks with different surface density and different thicknesses of TiO_2 coating. **g** Optical transmittances of the AgNW networks with different thicknesses of TiO_2 coating; the surface density of AgNW networks were 13.3 μg/cm^2.

successful coated on the surface of AgNWs. This phenomenon also confirmed the three-dimensional conformal coatings of ALD technique on irregular surfaces. And the corresponding surface morphologies as well as the roughness of these films were further estimated using AFM (Figure S2), showing a significantly decreasing roughness with modification of TiO_2 coating layer. Specifically, the root-mean-squared (RMS) values of surface roughness were 44.6 ± 2.3 nm, 22.6 ± 1.6 nm, 18.9 ± 1.3 nm and 8.74 ± 0.8 nm for the samples of the bare AgNW network, AgNWs@30 nm TiO_2, AgNWs@50 nm TiO_2 and AgNWs@80 nm TiO_2, respectively. It was clearly that the TiO_2 coating can reduce the surface roughness of AgNW networks, which should provide benefits for the fabrication of flexible devices. To further confirm the deposition of TiO_2 coating layer, the cross-sectional image and the EDS maps of AgNWs@30 nm TiO_2 were measured and illustrated in Figs. 2e and S3. It can be found that the AgNWs were isotropically coated with TiO_2 thin film of around 30 nm. Besides, the surface of PDMS substrate also achieved continuous and uniform deposition of TiO_2, which might increase the adhesion of AgNW networks on the substrate due to the infiltration and combination of TiO_2 films with the free volume in the subsurface regions of the PDMS [38].

It is crucial to balance the conductivity and optical transmittance of AgNW networks because they constrain each other [39]. The optical transmittance and electrical conductivity were further optimized via the density of AgNW networks. Different surface densities were obtained by changing the concentration of AgNWs ink. Figure 2f shows the sheet resistances of the AgNW networks at different surface densities. It was obvious that the sheet resistance decreased with the increase of the AgNWs surface density, due to more overlap and connection probability between AgNWs. It was also found that the TiO_2 coating layer affected the sheet resistances of AgNW networks, less than 20% of sheet resistances increased when the thicknesses of the TiO_2 coating layer were less than 80 nm. And with the increase of TiO_2 thickness, the sheet resistances of AgNW networks increased slightly, whose conductivity was well. This phenomenon might be attributed to the diffusion of Ag atoms through the semiconductor metal oxide [25, 40]. When the thickness of the metal oxide was thin, Ag atoms would diffuse through the coating, resulting in the network failure. On the contrary, when a large stress was applied, AgNW electrical resistance increased. Therefore, the sheet resistances of AgNW networks is related to the metal oxide thickness.

Since the silver is nearly opaque to light, higher surface density of AgNW network would lead to the lower optical transmittance. Considering the results of Figs. 2f and S4, the surface density of AgNW networks that applied in the subsequent studies was 13.3 μg/cm^2, which showed surface resistance of 20.8 ± 1.0 Ω/sq and optical transparency of around 80% in the visible range. In addition, the effect of the TiO_2 coating on optical transparency was also tested, as shown in Fig. 2g, from which, it can be seen that the optical transmittance of AgNW networks decreased with the increase of the TiO_2 coating thickness. However, the optical transparency of the flexible TCEs could still remain about 70% under the coating thickness of 80 nm.

Enhancement of mechanical reliability and environmental stability of AgNW networks with TiO_2 coatings

To investigate the mechanical properties of AgNWs/TiO_2 composites for flexible TCEs, the adhesion of AgNWs to the substrate was investigated. It was puzzled that AgNW networks without additional treatments tended to be easily removed from the substrate by a gentle wiping force. In order to evaluate the effects of TiO_2 coating on the adhesion of AgNW networks, both bare AgNW networks and the AgNW networks with TiO_2 coatings were subjected to ultrasonic concussion. Figure 3a shows that the sheet resistance of the bare AgNW networks increased remarkably due to ultrasonic concussion induced stripping, while the sheet resistance of AgNW networks with TiO_2 coatings changed slightly after ultrasonic concussion for 2 h. Peeling tests were also conducted for further verification of the adhesion enhancement with of AgNW networks with TiO_2 coatings, as shown in Fig. 3b. It was found that the sheet resistances of AgNWs with TiO_2 coating layers remained nearly unchanged after 10 cycles of peeling using 3 M tape, while the sheet resistance of the bare AgNW networks decreased rapidly owe to the constant peeling of AgNWs (shown in the inset). Both the ultrasonic concussion and 3 M tape peeling tests confirmed the strengthen effect of adhesion with TiO_2 coating layer.

The enhancements of mechanical reliability of the AgNWs/TiO_2 composites for flexible TCEs were investigated by bending tests and uniaxial tensile straining tests, the photographs of the testing process were shown in Figure S5. After 500 cycles of bending tests, both the bare AgNWs and AgNWs@30 nm TiO_2 still kept the good sheet resistances, as shown in Fig. 3c. However, AgNWs with thicker TiO_2 coatings over 50 nm would decrease the bending performance of AgNW networks. This phenomenon might be attributed to the rigid feature of inorganic material TiO_2, which is prone to cracks due to the existence of film stress when it is bent, and with the increase of inorganic material thickness, the maximum stress of the films increases, leading to the cracks in the AgNW/TiO_2 composites with TiO_2 coatings over 50 nm after repeated bending. The insert SEM image shows the cracks in the TCEs of AgNWs@50 nm TiO_2 after 500 bending cycles. In addition, the conductivity under uniaxial tensile straining test were also measured, as shown in Fig. 3d. It can be seen that the AgNW networks coated with thinner TiO_2 layer had more stable sheet resistances under tensile states. Therefore, it could be concluded that an appropriate thickness of about 30 nm TiO_2 coating layer can not only effectively enhance the adhesion of AgNWs on the substrate, but also improve the mechanical reliability.

In practical application, the thermal stability of AgNWs is also a major problem. The effects of TiO_2 coatings on the thermal stability of AgNW networks were also investigated as a function of the thickness of TiO_2 coating layer. The samples used for the tests were also fabricated with the surface density of 13.3 μg/cm^2. The thermal stability of AgNW networks with and without TiO_2 coatings was tested from 40 to 300 ℃ at a heating rate of 5 ℃/min. The initial sheet resistances of all the samples were nearly constant regardless of the thickness of TiO_2 coating layer, indicating that TiO_2 coating has little effect on the surface resistance of AgNW networks. It is shown in Fig. 4a that the surface resistance remained unchanged when the heating temperatures were less than 180 ℃. As the temperature further increased, the sheet resistances of the

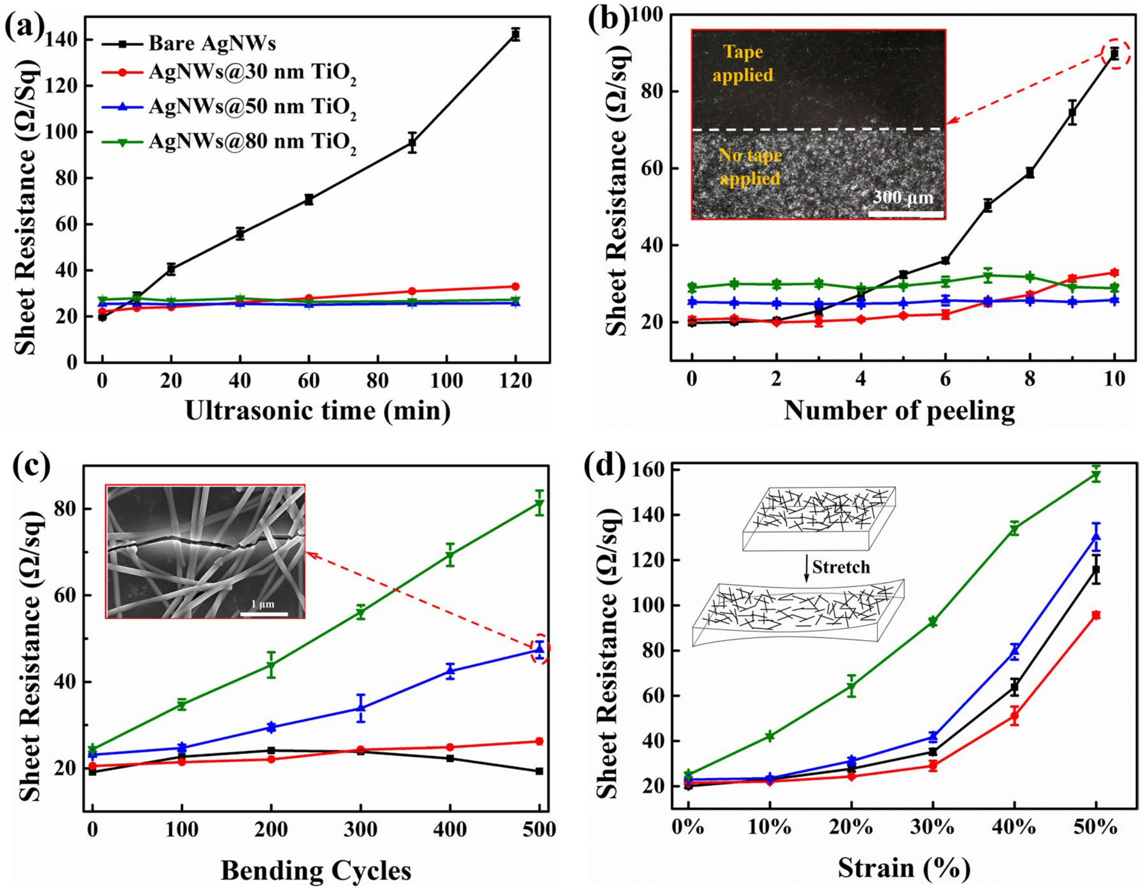


Figure 3 Adhesion and mechanical reliability of AgNWs/TiO_2 composites on PDMS for flexible TCEs: **a** by ultrasonic agitation (power = 500 W); **b** by 3 M tape peeling, the insert image shows the bare AgNW networks after 10 cycles of peeling test; **c** by cyclic bending test with bending radius of 5 mm, the insert image shows the TCEs of AgNWs@50 nm TiO_2 after 500 cycles of bending test; **d** by uniaxial tensile straining test, the insert diagrams show the testing process.

bare AgNW networks increased, while the sheet resistances of AgNW networks with TiO_2 coating can stand against the change up to 240 ℃, and then suffered from a sharp increase. It was found that this drastic change had already destroyed the conductive networks of AgNW, as shown in Fig. 4c–d. This phenomenon was attributed to the Plateau–Rayleigh instability [41]. The spheroidization of the bare AgNWs leaded to the disconnection of the conductive network, as shown in Fig. 4c, whereas Fig. 4d shows that the sample of AgNWs@30 nm TiO_2 retained the wirelike construction after the Plateau-Rayleigh instability, which also confirmed that the TiO_2 coating could improve the thermal endurance of AgNW networks. What's more, the barrier property of TiO_2 coating was accessed because AgNWs were easily oxidized by oxygen and water vapor. The oxidation stability test was carried by monitoring the conductance of AgNWs in a controlled environment of 85 ℃ and 85% RH, the results were plotted as normalized conductance (R/R_0) *vs.* time curves, as shown in Fig. 4b. As expected, the AgNW networks were effective encapsulated by a TiO_2 coating layer. Although the resistances of AgNWs/TiO_2 composites showed a subtle linear increase in the testing process, this phenomenon could be explained by the interaction of electron and phonon because of the long-time exposure to high temperature and humidity environment [42]. However, the bare AgNW networks showed the constant increase in resistance day by day. It was found that the surface of bare AgNWs generated many nano-particles after oxidation in a controlled environment of 85 ℃ and 85% RH for 30 days, as shown in Fig. 4e. It can be deduced that a non-conductive silver oxide layer was formed on the surface of bare AgNWs.

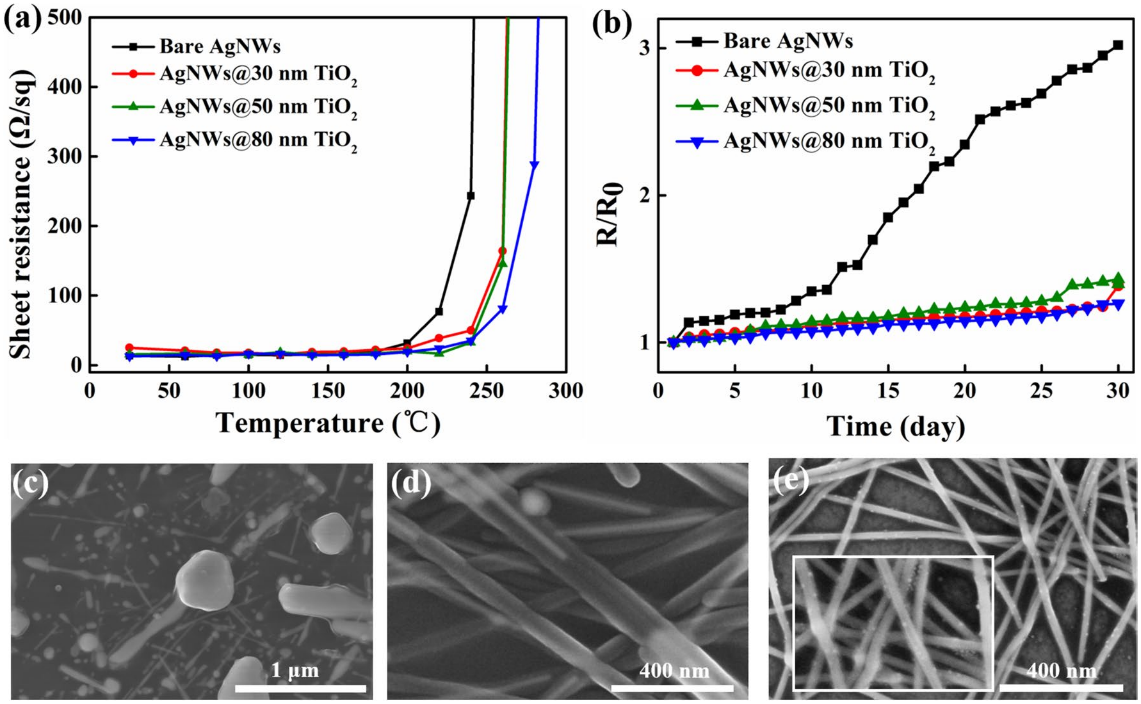


Figure 4 **a** Thermal stability of AgNW networks with and without TiO_2 coatings under different temperatures. **b** Dependence of the normalized conductance *vs.* time for AgNW networks with and without TiO_2 coatings in a controlled environment of 85 ℃ and 85% RH. SEM images of TCEs after stability test: **c** bare AgNWs heating at 250 ℃ for 15 min; **d** AgNWs@30 nm TiO_2 heating at 250 ℃ for 15 min; **e** bare AgNWs oxidation in a controlled environment of 85 ℃ and 85 RH for 30 days.

Patterning of AgNWs/TiO_2 composites and the application to the ACEL devices.

To further applied the flexible TCEs in reality, the patterned method of TCEs should be explored. According to the adhesion enhancement of AgNW networks to the substrate by TiO_2 coatings, a simple method based on photolithography and ultrasonic concussion processes was carried out to obtain the patterned AgNW/TiO_2 composites with various graphics, and finally AgNW/TiO_2 composites were applied as TCEs for ACEL devices. The fabricating processes were concretely shown in Fig. 1.

In this work, TCEs with the graphics of a snail and strip electrodes were successfully fabricated and used for ACEL devices, as the displays, respectively, shown in Figs. 5a, b and S6. It could be seen that the ACEL devices equably display the graphics, which illustrate the excellent conductivity of the patterned TCEs. The microscope image of Fig. 5c shows the TCEs with the strip width of 200 μm, the surface of the electrode was flat without defects. The changing of the sample in the ultrasonic concussion process was shown in Fig. S1. It could be seen that positive photoresist (PR) together with the bottom AgNW networks, detached from the PDMS substrate after 5 min ultrasonic concussion. After 30 min ultrasonic concussion, the pattern PR layer was all peeled off from the substrate, so that the strip TCEs were successfully fabricated. Besides, from the thickness measurement in Fig. 5d, the thickness of the AgNW/TiO_2 composites was about 120 ± 7.3 nm, it is worth mentioned that the strip TCEs show sharp and clearly edges. These results demonstrate the successful preparation of the patterned TCEs under the cooperation of photolithography, TiO_2 coating and ultrasonic concussion processes, which was greatly attributed to enhancement effects of TiO_2 coatings. Furthermore, the patternings of TCEs were also investigated by the way of traditional etching. After the photolithography process of Fig. 1, the AgNW networks were etched by dilute nitric acid. It was found that the strip widths of TCEs were all below the designing width of 200 μm, as the results shown in Fig. 5e. Because of the strong corrosivity of nitric acid, the etching would be quickly taken in the edge of the strip electrodes even if the protection by PR layer, while the ultrasonic concussion process could maintain the target graphics of TCEs, as Fig. 5f has

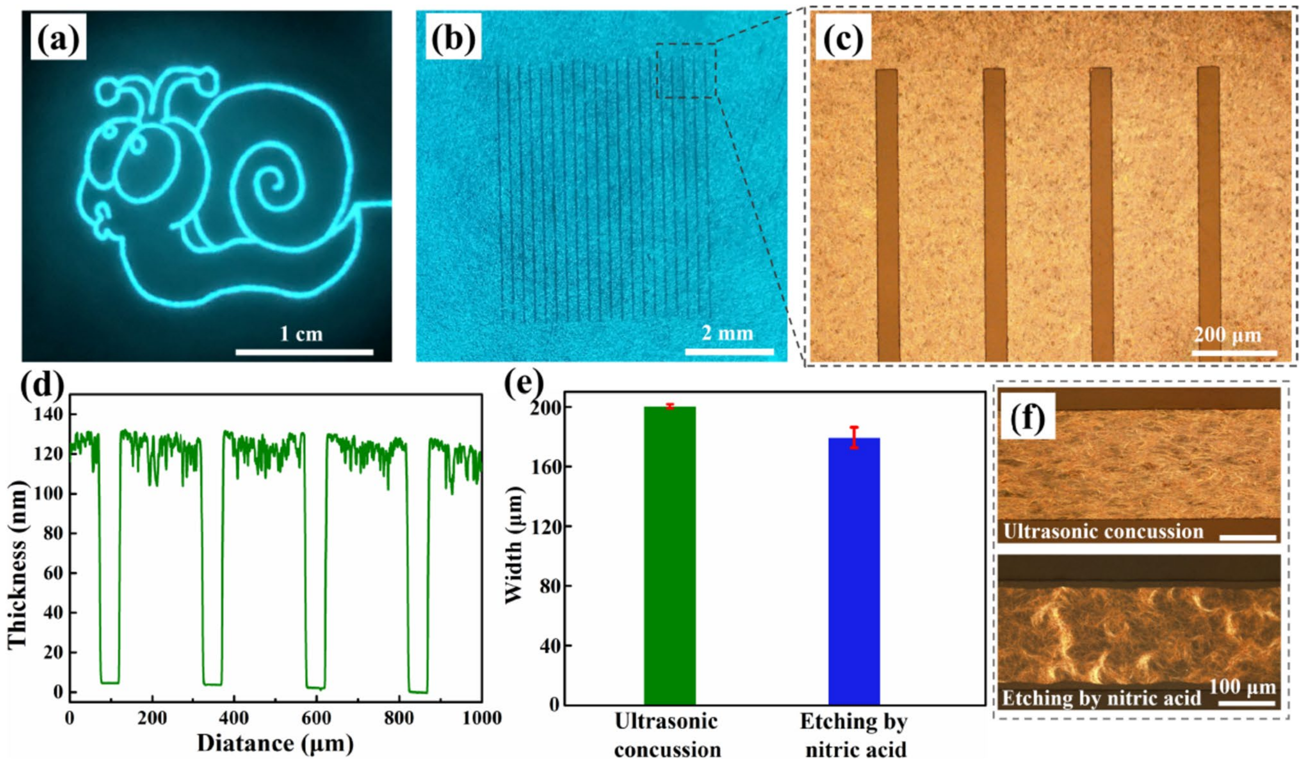


Figure 5 Photographs of the ACEL devices based on patterned TCEs: **a** a snail, **b** electrode with the strip width of 200 µm. **c** Microscope images of TCEs after 30 min ultrasonic concussion. **d** Thickness measurement to the sample of Fig. 5(c). **e** The width of strip TCEs fabricated by ultrasonic concussion and etching, the design widths both were 200 µm. **f** The corresponding microscope images of the strip TCEs after fabrication by ultrasonic concussion and etching.

shown. Thus, the patterning of AgNW/TiO_2 composites by ultrasonic concussion process was more easily to control compared to the traditional etching method.

The application of the AgNW/TiO_2 composites on ACEL devices indicates a potential value for the development of flexible electronics. Therefore, mechanical reliability and stability of the ACEL devices should be checked. To verify the mechanical reliability, the ACEL devices were tested under bending and compression states. As the results of Fig. 6a has shown, the devices based on patterned TCEs of AgNWs@30 nm TiO_2 and bare AgNWs, both has excellent emission properties after 500 cycles bending tests with the bending radius of 5 mm, while the TCEs of AgNWs@30 nm TiO_2 showed a little superior than the bare AgNW networks. In the insert image, it is shown that the ACEL devices can maintain uniform emission under different deformation states. These excellent performances were mainly attributed to the highly stable and flexible AgNW/TiO_2 composites. While under the uniaxial compression tests, the devices based on patterned TCEs of AgNWs@30 nm TiO_2 and the bare AgNW networks show the same trends in the changes of luminance, as shown in Fig. 6b. The luminance increased as the increase in compression ratio. This was because that the thickness of EL layer decreased in compressed area, which leaded to the enhancement of electrical field between the top and bottom electrodes [43]. Thus, it was concluded that the ACEL device based on patterned TCEs of AgNWs@30 nm TiO_2 could showed excellent mechanical properties. In addition, the degradation tests of ACEL devices were also investigated. As predicted from the result of AgNWs oxidation test, the lifetime of ACEL device could be prolonged by using the TCEs with TiO_2 coating layer. It was found from the results of Fig. 6c, the ACEL device based on TCEs of AgNWs@30 nm TiO_2 kept good emission property after degradation test in a controlled environment of 85 ℃ and 85% RH for 30 days. However, the luminance of the ACEL device based on bare AgNWs decreased day by day. It is reasonable to infer that the lifetime of ACEL device mainly depends on the electrodes, consequently the barrier performance of TiO_2 coating layers improved the lifetime of ACEL device. Because of the high optical

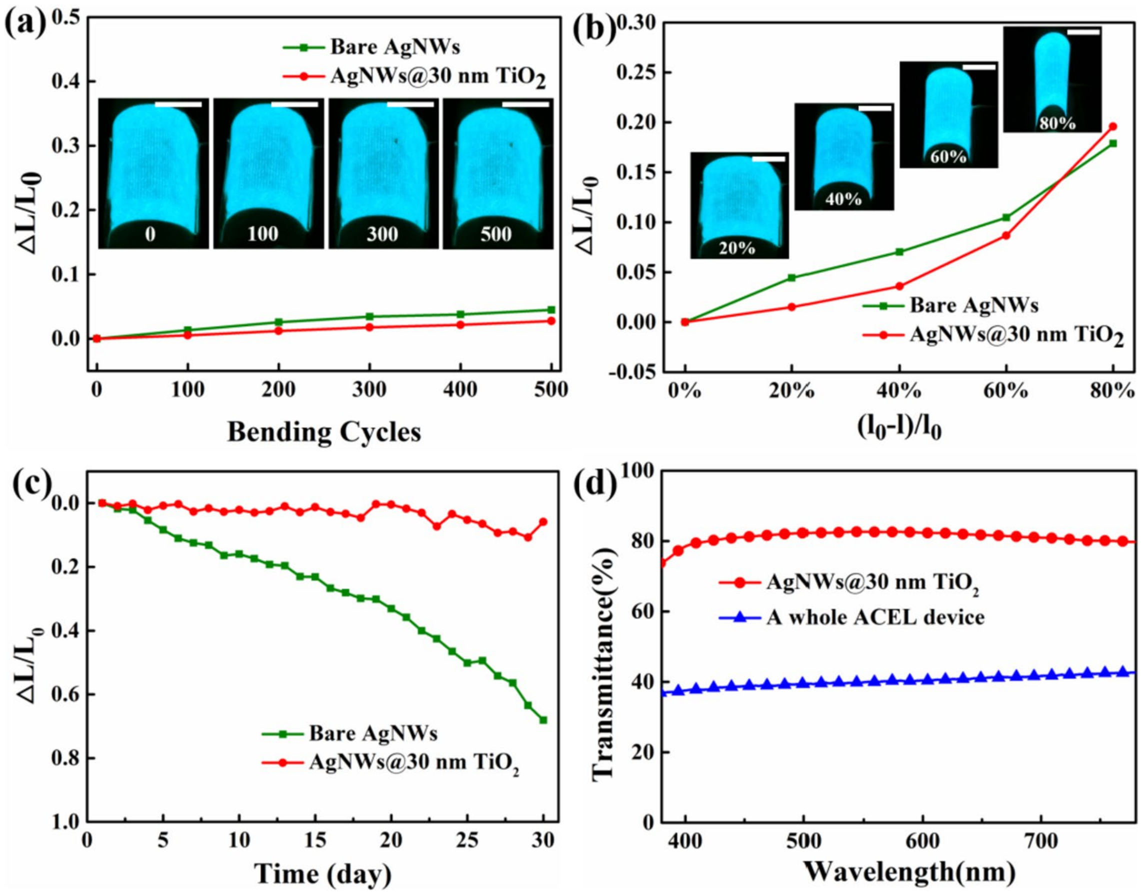


Figure 6 **a** The normalized luminance of the ACEL device after the bending test with bending radius of 5 mm; the insert images show the devices (based on patterned TCEs of AgNWs@30 nm TiO_2) after 0, 100, 300 and 500 bending cycles, the scale bar is 5 mm. **b** The normalized luminance of the ACEL device under different uniaxial compression ratios; the insert images show the devices (based on patterned TCEs of AgNWs@30 nm TiO_2) under the compression ratios of 20%, 40%, 60% and 80%, the scale bar is 5 mm. **c** Dependence of the normalized luminance vs. time of the ACEL devices in a controlled environment of 85 ℃ and 85% RH. **d** The transparency of an ACEL device based on the TCE of AgNWs@30 nm TiO_2.

transparency, AgNW/TiO_2 composites are more attractive. As Fig. 6d has shown, the transparency of the whole ACEL device was around 40%, and the display images before and after applying an alternating voltage can be clearly seen from the photographs in Figure S8. These features indicate the prospects of the AgNW/TiO_2 compisites on applications to flexible electronics.

Conclusions

In summary, based on the conformal TiO_2 coatings by atomic layer deposition (ALD), highly stable and patterned AgNW/TiO_2 composites were successfully fabricated for flexible transparent conductive electrodes (TCEs). TiO_2 coatings were introduced for the stability enhancement of AgNW networks. The measurements were conducted to determine the effects of the thickness of TiO_2 coating on the mechanical property and stability of AgNW networks. It was found that TiO_2 coating could not only enhance the adhesion of AgNWs to the substrate, but also improve the flexibility of AgNW networks. This was attributed to the three-dimensional conformal deposition of ALD technique on irregular surfaces, so that the surface of AgNWs and the substrate were coated with a uniform and conformal TiO_2 thin film. Meanwhile, the thermal and oxidation stabilities of AgNW networks could be greatly improved because of the barrier performance of TiO_2 coating layers. Besides, based on the adhesion enhancement by conformal TiO_2 coating layers, a novelty patterning method of the AgNW networks were implemented by cooperating with photolithography and ultrasonic concussion process. The strip electrodes with the low width of 200 μm were well patterned, showing sharp edges without defects. At last, highly stable patterned AgNW/TiO_2 composites were successfully applied as TCEs to alternating current electroluminescent (ACEL) devices. The graphics of ACEL display could be design as needed, and the whole ACEL device showed a high transparency of around 40%. As expected, the flexibility and the lifetime of ACEL devices were correspondingly improved owe to the enhancement by TiO_2 coatings. These results proved that the highly stable patterned AgNW/TiO_2 composites could be excellent TCEs for flexible or wearable electronics.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 62204089), the Scientific Research Funds of Huaqiao University (21BS132), the Promotion Program for Young and Middle-aged Teacher in Science and Technology Research of Huaqiao University (ZQN-1124) and the National Key R&D Program of China (No.2021YFB3600104).

Author contributions

YW: Conceptualization, Data curation, Validation, Writing—Original draft preparation, Experimental operation, Reviewing and Editing. GC: Experimental operation, Sample measurement and Analyze. XZ: Conceptualization, Supervision, Reviewing and Editing, Project administration. YZ: Investigation and Supervision. QY: Supervision, methodology, Reviewing. TG: Supervision and Validation.

Data availability

Data will be made available on request.

Declarations

Conflict of interest The authors declare no conflict of interest.

Ethical approval Not applicable.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10853-023-09152-5.

References

[1] Qiu T, Luo B, Akinoglu EM, Yun JH, Gentle IR, Wang L (2020) Trilayer nanomesh films with tunable wettability as highly transparent, flexible, and recyclable electrodes. Adv Funct Mater 30:2002556. https://doi.org/10.1002/adfm.202002556

[2] Fan Q, Miao J, Liu X, Zuo X, Zhang W, Tian M, Zhu S, Qu L, Zhang X (2022) Biomimetic hierarchically silver nanowire interwoven MXene mesh for flexible transparent electrodes and invisible camouflage electronics. Nano Lett 22:740–750. https://doi.org/10.1021/acs.nanolett.1c04185

[3] Kim SY, Shin WH, Kim HS, Jung DW, Kim MJ, Kim K, Roh JW, Hwang S, Lee J, Yang D, Sohn H, Kim SH, Jung C, Cho E, Yun DJ, Kim J, Cho YJ, Kim SI, Lee KH, Kwak C, Ko DS (2021) Silver nanowire network hybridized with silver nanoparticle-anchored ruthenium oxide nanosheets for foldable transparent conductive electrodes. ACS Appl Mater Interfaces 13:11396–11402. https://doi.org/10.1021/acsami.0c19471

[4] Zhang C, Anasori B, Seral Ascaso A, Park SH, McEvoy N, Shmeliov A, Duesberg GS, Coleman JN, Gogotsi Y, Nicolosi V (2017) Transparent, flexible, and conductive 2D titanium carbide (MXene) films with high volumetric capacitance. Adv Mater 29:1702678. https://doi.org/10.1002/adma.201702678

[5] Lin Y, Li Q, Ding C, Wang J, Yuan W, Liu Z, Su W, Cui Z (2022) High-resolution and large-size stretchable electrodes based on patterned silver nanowires composites. Nano Res 15:4590–4598. https://doi.org/10.1007/s12274-022-4088-x

[6] Li P, Zhang Y, Zheng Z (2019) Polymer-assisted metal deposition (PAMD) for flexible and wearable electronics: principle, materials, printing, and devices. Adv Mater 31:1902987. https://doi.org/10.1002/adma.201902987

[7] Zhang S, Li S, Xia Z, Cai K (2020) A review of electronic skin: soft electronics and sensors for human health. J Mater Chem B 8:852–862. https://doi.org/10.1039/c9tb02531f

[8] Herbert R, Kim JH, Kim YS, Lee HM, Yeo WH (2018) Soft material-enabled, flexible hybrid electronics for medicine, healthcare, and human-machine interfaces. Materials 11:187. https://doi.org/10.3390/ma11020187

[9] Fan X (2021) Doping and design of flexible transparent electrodes for high-performance flexible organic solar cells: recent advances and perspectives. Adv Funct Mater 31:2009399. https://doi.org/10.1002/adfm.202009399

[10] Zhu H, Shen Y, Li Y, Tang J (2018) Recent advances in flexible and wearable organic optoelectronic devices. J Semicond 39:011011. https://doi.org/10.1088/1674-4926/39/1/011011

[11] Park JH, Hwang GT, Kim S, Seo J, Park HJ, Yu K, Kim TS, Lee K (2017) Flash-induced self-limited plasmonic welding of silver nanowire network for transparent flexible energy harvester. Adv Mater 29:1603473. https://doi.org/10.1002/adma.201603473

[12] Zhou W, Yao S, Wang H, Du Q, Ma Y, Zhu Y (2020) Gas-permeable, ultrathin, stretchable epidermal electronics with porous electrodes. ACS Nano 14:5798–5805. https://doi.org/10.1021/acsnano.0c00906

[13] Lin Y, Yuan W, Ding C, Chen S, Su W, Hu H, Cui Z, Li F (2020) Facile and efficient patterning method for silver nanowires and its application to stretchable electroluminescent displays. ACS Appl Mater Interfaces 12:24074–24085. https://doi.org/10.1021/acsami.9b21755

[14] Liu GS, Xu Y, Kong Y, Wang L, Wang J, Xie X, Luo Y, Yang BR (2018) Comprehensive stability improvement of silver nanowire networks via self-assembled mercapto inhibitors. ACS Appl Mater Interfaces 10:37699–37708. https://doi.org/10.1021/acsami.8b13329

[15] Liu GS, Zheng H, Zeng Z, Wang Y, Guo W, Wang T, Chen H, Chen Y, Hu S, Chen L, Chen Y, Xie W, Yang BR, Luo Y (2022) Self-assembled monolayer modulated Plateau–Rayleigh instability and enhanced chemical stability of silver nanowire for invisibly patterned, stable transparent electrodes. Nano Res 15:4552–4562. https://doi.org/10.1007/s12274-021-4042-3

[16] Zilberberg K, Gasse F, Pagui R, Polywka A, Behrendt A, Trost S, Heiderhoff R, Goerrn P, Riedl T (2014) Highly robust indium-free transparent conductive electrodes based on composites of silver nanowires and conductive metal oxides. Adv Funct Mater 24:1671–1678. https://doi.org/10.1002/adfm.201303108

[17] Bai S, Wang H, Yang H, Zhang H, Chen T, Guo X (2018) Fused silver nanowires with silica sol nanoparticles for smooth, flexible, electrically conductive and highly stable transparent electrodes. RSC Adv 8:13466–13473. https://doi.org/10.1039/c8ra01569d

[18] Zhu R, Chung CH, Cha KC, Yang W, Zheng YB, Zhou H, Song TB, Chen CC, Weiss PS, Li G, Yang Y (2011) Fused silver nanowires with metal oxide nanoparticles and organic polymers for highly transparent conductors. ACS Nano 5:9877–9882. https://doi.org/10.1021/nn203576v

[19] Ricciardulli AG, Yang S, Wetzelaer GJAH, Feng X, Blom PWM (2018) Hybrid silver nanowire and graphene-based solution-processed transparent electrode for organic optoelectronics. Adv. Funct. Mater. 28:1706010. https://doi.org/10.1002/adfm.201706010

[20] Zhang G, Wu H, Wang X, Wang T, Liu C (2016) Transparent capacitors with hybrid ZnO: Al and Ag nanowires as electrodes. Nanotechnology 27:105204. https://doi.org/10.1088/0957-4484/27/10/105204

[21] Jiang Y, Li M, Chen C, Xue Z, Xie X, Zhou X, Mai YW (2018) Effect of elastic modulus mismatch of epoxy/titanium dioxide coated silver nanowire composites on the performance of thermal conductivity. Compos Sci Technol 165:206–213. https://doi.org/10.1016/j.compscitech.2018.06.028

[22] Ali K, Duraisamy N, Kim CY, Choi KH (2014) Al_2O_3 coatings fabrication on silver nanowires through low temperature atomic layer deposition. Mater Manuf Process 29:1056–1061. https://doi.org/10.1080/10426914.2014.930959

[23] Viet Huong N, Resende J, Papanastasiou DT, Fontanals N, Jimenez C, Munoz-Rojas D, Bellet D (2019) Low-cost fabrication of flexible transparent electrodes based on Al doped ZnO and silver nanowire nanocomposites: impact of the network density. Nanoscale 11:12097–12107. https://doi.org/10.1039/c9nr02664a

[24] Han X, Huang Y, Wang J, Zhang G, Li T, Liu P (2022) Flexible hierarchical ZnO/AgNWs/carbon cloth-based film for efficient microwave absorption, high thermal conductivity and strong electro-thermal effect. Compos Part B-Eng 229:109458. https://doi.org/10.1016/j.compositesb.2021.109458

[25] Aghazadehchors S, Viet Huong N, Munoz Rojas D, Jimenez C, Rapenne L, Ngoc Duy N, Bellet D (2019) Versatility of bilayer metal oxide coatings on silver nanowire networks for enhanced stability with minimal transparency loss. Nanoscale 11:19969–19979. https://doi.org/10.1039/c9nr05658k

[26] Song TB, Rim YS, Liu F, Bob B, Ye S, Hsieh YT, Yang Y (2015) Highly robust silver nanowire network for transparent

electrode. ACS Appl Mater Interfaces 7:24601–24607. https://doi.org/10.1021/acsami.5b06540

[27] Yeh MH, Chen PH, Yang YC, Chen GH, Chen HS (2017) Investigation of Ag–TiO_2 interfacial reaction of highly stable Ag Nanowire transparent conductive film with conformal TiO_2 coating by atomic layer deposition. ACS Appl Mater Interfaces 9:10788–10797. https://doi.org/10.1021/acsami.6b13070

[28] Hao T, Wang S, Xu H, Zhang X, Magdassi S, Pan L, Song Y, Li Y, Zhao J (2022) Novel transparent TiO_2/AgNW−Si(NH_2)/PET hybrid films for flexible smart windows. ACS Appl Mater Interfaces 14:21613–21622. https://doi.org/10.1021/acsami.1c25002

[29] Ramasamy P, Seo DM, Kim SH, Kim J (2012) Effects of TiO_2 shells on optical and thermal properties of silver nanowires. J Mater Chem 22:11651–11657. https://doi.org/10.1039/c2jm00010e

[30] Jang I, Kang T, Cho W, Kang YS, Oh SG, Im SS (2015) Preparation of silver nanowires coated with TiO_2 using chemical binder and their applications as photoanodes in dye sensitized solar cell. J Phys Chem Solids 86:122–130. https://doi.org/10.1016/j.jpcs.2015.07.005

[31] Kumari MGCM, Perera CS, Dassanayake BS, Dissanayake MAKL, Senadeera GKR (2019) Highly efficient plasmonic dye-sensitized solar cells with silver nanowires and TiO_2 nanofibres incorporated multi-layered photoanode. Electrochim Acta 298:330–338. https://doi.org/10.1016/j.electacta.2018.12.079

[32] Dong H, Wu Z, Lu F, Gao Y, El Shafei A, Jiao B, Ning S, Hou X (2014) Optics-electrics highways: plasmonic silver nanowires@TiO_2 core-shell nanocomposites for enhanced dye-sensitized solar cells performance. Nano Energy 10:181–191. https://doi.org/10.1016/j.nanoen.2014.09.011

[33] Hu L, Qi W, Li Y (2017) Coating strategies for atomic layer deposition. Nanotechnol Rev 6:527–547. https://doi.org/10.1515/ntrev-2017-0149

[34] Kwon JH, Jeon Y, Choi S, Park JW, Kim H, Choi KC (2017) Functional design of highly robust and flexible thin-film encapsulation composed of quasi-perfect sublayers for transparent, flexible displays. ACS Appl Mater Interfaces 9:43983–43992. https://doi.org/10.1021/acsami.7b14040

[35] Wang X, Zhao Z, Zhang C, Li Q, Liang X (2020) Surface modification of catalysts via atomic layer deposition for pollutants elimination. Catalysts 10:1298. https://doi.org/10.3390/catal10111298

[36] Tseng MH, Su DY, Chen GL, Tsai FY (2021) Nano-laminated metal oxides/polyamide stretchable moisture- and gas-barrier films by integrated atomic/molecular layer deposition. ACS Appl Mater Interfaces 13:27392–27399. https://doi.org/10.1021/acsami.1c03895

[37] Tseng JY, Lee L, Huang YC, Chang JH, Su TY, Shih YC, Lin HW, Chueh YL (2018) Pressure welding of silver nanowires networks at room temperature as transparent electrodes for efficient organic light-emitting diodes. Small 14:e1800541. https://doi.org/10.1002/smll.201800541

[38] Chen G, Weng Y, Wang W, Hong D, Zhou L, Zhou X, Wu C, Zhang Y, Yan Q, Yao J, Guo T (2021) Spontaneous formation of random wrinkles by atomic layer infiltration for anticounterfeiting. ACS Appl Mater Interfaces 13:27548–27556. https://doi.org/10.1021/acsami.1c04076

[39] Xie H, Yang X, Du D, Zhao Y, Wang Y (2018) Flexible transparent conductive film based on random networks of silver nanowires. Micromachines 9:295. https://doi.org/10.3390/mi9060295

[40] Khan A, Viet Huong N, Munoz Rojas D, Aghazadehchors S, Jimenez C, Ngoc Duy N, Bellet D (2018) Stability enhancement of silver nanowire networks with conformal ZnO coatings deposited by atmospheric pressure spatial atomic layer deposition. ACS Appl Mater Interfaces 10:19208–19217. https://doi.org/10.1021/acsami.8b03079

[41] Liu GS, He M, Wang T, Wang L, He Z, Zhan R, Chen L, Chen Y, Yang BR, Luo Y, Chen Z (2020) Optically programmable Plateau–Rayleigh instability for high-resolution and scalable morphology manipulation of silver nanowires for flexible optoelectronics. ACS Appl Mater Interfaces 12:53984–53993. https://doi.org/10.1021/acsami.0c11682

[42] Shanker R, Cho S, Choe A, Kim MP, Khan Z, Kang S, Ko H (2019) Solution-processable, high-performance flexible electroluminescent devices based on high-k nanodielectrics. Adv Funct Mater 29:1904377. https://doi.org/10.1002/adfm.201904377

[43] Bid A, Bora A, Raychaudhuri AK (2006) Temperature dependence of the resistance of metallic nanowires of diameter >= 15 nm: applicability of Bloch–Gruneisen theorem. Physical Review B 74:035426. https://doi.org/10.1103/PhysRevB.74.079903