High-Performance Silver Nanowire Flexible Transparent Electrodes under Current Stress and the Application for Long Lifetime OLEDs

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***Abstract*—This paper reports a long lifetime flexible OLED based on TiO_2 modified silver nanowire (AgNW) network flexible transparent electrode (FTE). For the AgNW@TiO_2 FTE, an ultrathin (2-5 nm), conformal, and continuous TiO_2 shell is coated around AgNWs by a facile and cost-effective solution-processed sol-gel method, which can significantly improve the stability of AgNWs under current stress. By embedding the AgNW network on polymer substrate, the surface roughness of FTEs reduced significantly. OLEDs were prepared by spin coating and evaporation techniques on indium-tin-oxide (ITO) electrodes and AgNW FTEs. As replacing ITO with AgNWs can improve the light-emitting efficiency, the OLEDs based on AgNW FTE can extend the lifetime. Besides, TiO_2 protective shell on AgNW network makes the devices working steadily. The lifetime of ITO-OLED, AgNW-OLED, AgNW@TiO_2-OLED are 200 min, 235 min, and 355 min, respectively.**

Keywords—OLED; Silver nanowire; Flexible transparent electrode

I. Introduction

Recently, organic light-emitting diodes (OLEDs), with high energy efficiency and low energy consumption, have been considered as a revolutionary alternative for next-generation flat panel displays and energy consumption [1]. With the increasing demand on flexible displays, the flexibility of OLEDs becomes a research hotspot for flexible optoelectronic systems [2].

Flexible transparent electrode (FTE) is the key component for flexible OLED. Indium-tin-oxide (ITO) is the most commonly used materials for fabricating FTE due to its high optical transmittance and electrical conductivity [3]. However, the flexibility of OLEDs based on ITO FTE is still a critical barrier to overcome for large-scale applications [4]. Because ITO is very fragile and usually broken during cyclic deformation [5]. Many alternatives have been proposed to replace ITO, including carbon nanotubes [6-7], graphene [8], poly(3,4-ethylenedioxythiophene)/poly(styrenesulfon) (PEDOT:PSS) [9-10], and silver nanowires (AgNWs) [11]. Among these materials, AgNW network, with excellent optoelectrical performance, mechanical flexibility, and solution-processability, seems to be the most promising candidate as a platform of the flexible devices [12-13]. Moreover, it is also worth pointing that the wave-guide mode can be effectively reduced, due to the existence of Ag NWs/polymer substrate, which prevents the total reflection in the case ITO electrode.

However, the lifetime of flexible OLED based AgNW network is difficult to reach the expected value, because nanoscale AgNWs usually suffer from poor stability when subjected to electrical stress [14]. For example, it has been reported that after a current density of 155 mA/cm^2 was applied in AgNW FTE, AgNWs has broken and the morphologies are similar to nanowires annealed at 200 ℃ [15]. Many attempts have been made to address this hard issue. Welding nanowires together can improve the electrical conductivity to reduce the Joule heat [16]. However, this method can only improve the electrical stability to some degree. Overcoat layer such as zinc oxide (ZnO) has been proved to be an effective method to improve electrical stability of AgNW network [15], but the involved atomic layer deposition (ALD) method is expensive and time-consuming.

Herein, this study reports a long-lifetime flexible OLED based on TiO_2 modified AgNW network FTE. An ultrathin (2-5 nm), conformal, and continuous TiO_2 shell was coated around AgNWs by facile and cost-effective solution-processed sol-gel method. The obtained AgNW@TiO_2 core-shell network can significantly enhance the electrical stability of AgNWs while maintaining a network structure. Moreover, the electrical conductivity and optical transmittance can also be improved at the same time. Thanks to these improvements, the lifetime of flexible OLED using AgNW@TiO_2 FTE is 1.8 times as much of that based on industrial ITO electrode, exhibiting the potential for next-generation optoelectronic system.

II. Materials and Methods

A. The preparation of AgNWs solution

Zhejiang Kechuang Advanced Mateirals Co., Ltd. provided the AgNWs, which had an average diameter of 30 nm and lengths in the range of 10—20 μm. Isopropyl alcohol (IPA), DI water, titanium isopropoxide, and hydrogen peroxide were purchased from Aladdin. All chemicals were used as received. The AgNWs were diluted with IPA to a concentration of 5 mg/mL.

B. Characterization

The microstructure of the prepared AgNW electrodes was observed by an FEI Helios Nanolab 600i scanning electron microscope and FEI Tecnai G2 F30 transmission electron microscope. The sheet resistance was tested by a M3 4-probe tester from Suzhou Lattice Electronics Co., LTD. The transmittance was measured using a Shimadzu Corporation ultraviolet−visible spectrophotometer.

III. Results and Discussion

A. The preparation of AgNWs@TiO_2 network

AgNWs were uniformly distributed onto glass substrate using a Mayer rod. As shown in Fig. 1(a), AgNWs are stacked onto each other and a conductive network is formed. To improve the electrical stability, TiO_2 layer was coated around AgNWs using our previous reported method [17]. Typically, the TiO_2 precursor solution was obtained by

dissolving titanium isopropoxide and hydrogen peroxide into DI water. After stirring, the obtained yellow gel was spin-coated onto the AgNW network. As shown in Fig. 1(b), the sample maintains network structure, and the TiO_2 precursor solution has no damage to the AgNWs. TEM images in Fig. 1(c) shows that an ultrathin, conformal, and continuous TiO_2 shell with a thickness of 2-5 nm was tightly wrapped onto AgNW network, forming core-shell structure. Fig. 1(d) shows the transmittance spectra (from 300 nm to 800 nm) of AgNW network and AgNW@TiO_2 network. Only slight change of spectra was observed, indicating the TiO_2 layer has a tiny effect on the transmittance. Surprisingly, the transmittance slightly increased from 500 nm to 800 nm after coating TiO_2 layer, which can be attributed to the fact that TiO_2 layer has a negligible on the absorption of AgNW network but can significantly reduce the scattering of AgNW surface. Moreover, the electrical conductivity can also be improved after TiO_2 sol treatment. The sheet resistance of the pristine AgNW network is 8 Ohm/sq at a transmittance of 85.4% (at 550 nm). By contrast, the sheet resistance decreased to 7.2 Ohm/sq and the transmittance increased to 86.1%. The improvement of electrical conductivity is caused by the shrinking force produced by TiO_2 precursor decomposition, which can tighten the stacked AgNWs and enlarge the contact area.

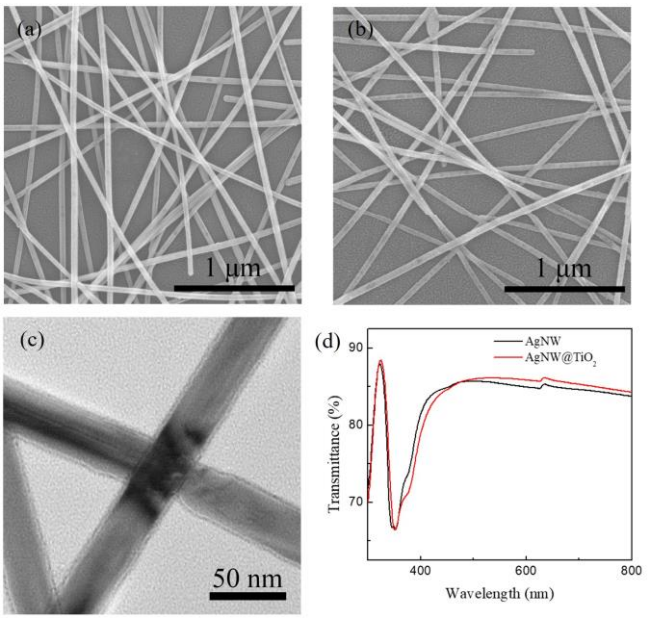

Fig. 1. (a) SEM image of AgNW network, (b) SEM iamge of AgNW@TiO_2 network, (c) TEM image of AgNW@TiO_2 network, (d) Transmittance of AgNW network and AgNW@TiO_2 network

B. *Improved current stability of AgNWs@TiO_2 network*

For the applications in OLEDs, AgNW network will be subjected to continuous current stress. We in-situ measured the change of resistance of AgNW network and AgNW@TiO_2 network under current density at 150 mA/cm^2. As shown in Fig. 2(a), the resistance of pristine AgNW network rapid increased. After the current stress was applied for 10 min, the resistance is out of the measuring range, suggesting it has lost conductivity and failed. In contrast, the resistance of AgNW@TiO_2 network remained stable after 30 min under the same condition, indicating the improved electrical stability. The morphologies of AgNW network and AgNW@TiO_2 network after applying current stress were also characterized using SEM, as shown in Fig. 2(b) and (c). It is obviously observed that the pristine AgNWs have been damaged and disconnected. However, the AgNW@TiO_2 network remains intact. The results are also consistent with the change of resistance. The enhancement of TiO_2 protective layer can be attributed two aspects. On the one hand, as mentioned above, the conductivity is improved. According to Joule's law, smaller Joule heat will be generated when the resistance decreased under the same current density. On the other hand, the compact TiO_2 layer can effectively wrapped around AgNWs, preventing the its damage under current stress.

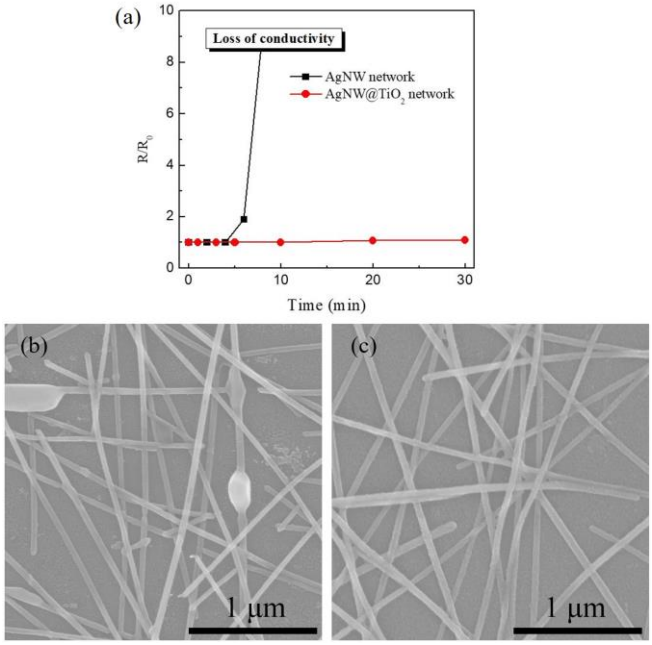

Fig. 2. (a) Relative resistance of AgNW network and AgNW@TiO_2 network, (b) SEM of AgNW network after electrical stressing for 10 min, (c) SEM of AgNW@TiO_2 network after electrical stressing for 30 min

C. *The preparation process of AgNW@TiO_2 FTE*

High surface roughness is easily caused the short circuit of flexible OLEDs. Because the thickness of the organic layer is nanometer, the surface roughness of the FTE needs to be at nanoscale. In order to reduce the surface roughness of AgNW FTE, we embedded the AgNW network into polymer substrate. Fig. 3(a) shows the schematic diagram of preparing AgNW network FTE will embedding structure. Firstly, AgNW network was coated onto the surface of the glass substrate using the Meyer bar method. Then, PI tape with a thickness of 90 μm was adhered on both sides of the glass substrate, and a clean glass substrate without coating AgNWs was placed. A 90 μm gap was formed between these two glass substrates. Subsequently, the polymer precursor will enter the gap under the driving of high capillary force. Finally, the polymer precursor was cured by UV machine. At last, the FTE was peeled off from the glass substrate [18].

To quantitatively analyze the surface state, we measured the surface roughness of AgNW FTE and AgNW@TiO_2 FTE using by a AFM machine, as shown in Fig. 3(b). The surface roughness of AgNW TFE and AgNW@TiO_2 FTE are 2.6 nm and 1.9 nm, respectively. Obviously, the surface roughness of both is at nanoscale, suggesting the embedding structure can effectively improve the flatness of FTEs. By contrast with AgNW FTE, the lower surface roughness of

AgNW@TiO_2 FTE can be ascribed to the fact that TiO_2 can fill the gap between nanowires.

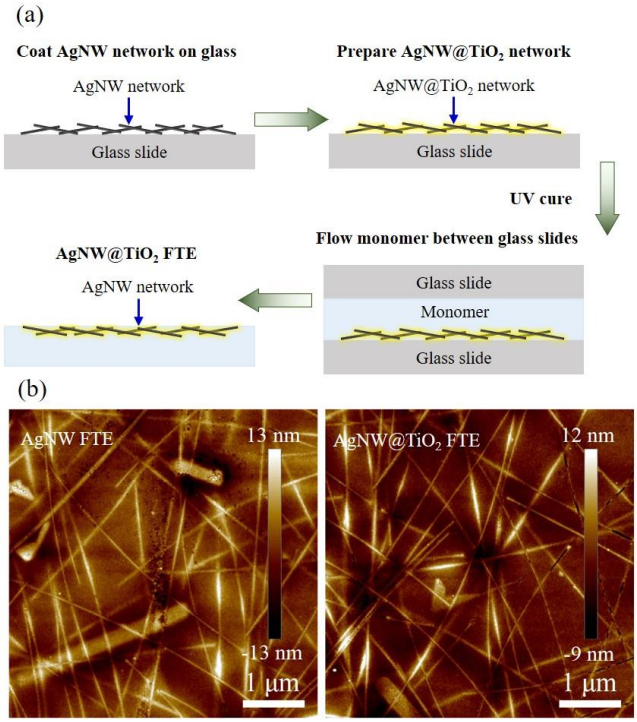

Fig. 3. (a) The preparation process of AgNW@TiO_2 FTE, (b) AFM image of AgNW FTE and AgNW@TiO_2 FTE

D. *The luminous efficiency of OLEDs*

The OLEDs on ITO electrode, AgNW FTE, and AgNW@TiO_2 FTE were prepared using our previous process [18]. Fig. 4(a) shows the current density (J) and luminance of OLED as functions of voltage. At the same voltage, the current density of AgNW-OLED and AgNW@TiO_2-OLED is similar, indicating that TiO_2 protective shell has negligible effect on the transfer of electron, while the current density of ITO-OLED is several times higher. For example, when voltage of 6 V was input, the current density of ITO-OLED is 229 mA/cm^2, while that of AgNW-OLED is 76 mA/cm^2. The work function of PEDOT:PSS, ITO, and AgNWs is 5.2 eV, 4.8 eV, and 4.2 eV, respectively. Obviously, the difference of work function between PEDOT:PSS and AgNWs is larger than that between PEDOT:PSS and ITO, which would increase the resistance of hole injection. Therefore, under the same voltage, AgNW-OLED has a lower current density. When the voltage is low, the brightness of ITO-OLED is higher. However, when the voltage is near 6 V, the brightness of AgNW-OLED is slightly higher than that of ITO-OLED. Fig. 4(b) shows the current efficiency and power efficiency of OLED changing with brightness. It can be observed that the current efficiency and power efficiency of ITO-OLED, AgNW-OLED, and AgNW@TiO_2-OLED increased in order. When the brightness is 1000 cd/m^2, the current efficiency and power efficiency of ITO-OLED, AgNW-OLED, and AgNW@TiO_2-OLED are 45.5 cd/A and 44.8 lm/W, 77.4 cd/A and 55.1 lm/W, and 74.6 cd/A and 59.7 lm/W, respectively. It can be concluded that replacing ITO with AgNWs can improve the light-emitting efficiency of OLED, and coating TiO_2 protective shell on silver nanowires has negligible effect on the light-emitting efficiency of OLED.

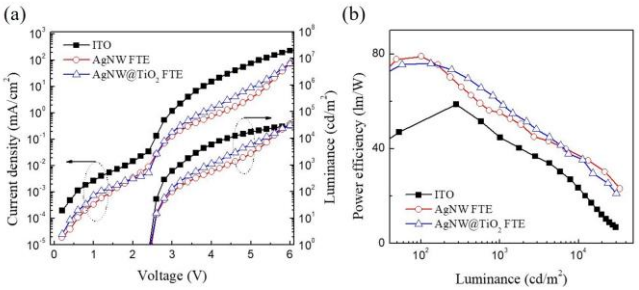

Fig. 4. (a) Current density-voltage-luminance characterizations, (b) power efficiency-luminance-current efficiency characterizations

E. *The lifetime of OLEDs*

The organic light-emitting layer in OLED can convert the carrier energy into photons. However, when constant voltage was inputted, the efficiency of converting carriers into photons in the organic light-emitting layer will gradually decrease, resulting in the decrease of luminance. In this work, the time it takes for the OLED luminance to decay from 5000 cd/m^2 to 2500 cd/m^2 is defined as the lifetime of the OLED ($t_{1/2}$). Fig. 5 shows the lifetime of OLED based on different FTEs. The lifetime of ITO-OLED, AgNW-OLED, AgNW@TiO_2-OLED are 200 min, 235 min, and 355 min, respectively.

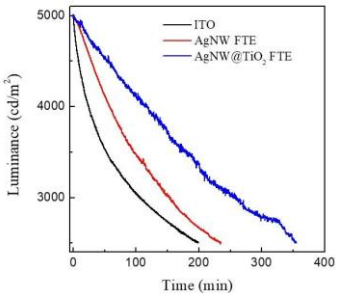

Fig. 5. Variation of luminance as a function of time

Fig. 6(a) shows the variation of power efficiency as a function of working time. It can be seen that the power efficiency of OLED gradually decreases with the deterioration of light-emitting layer. The rate of degradation in OLEDs is proportional to the current density squared [19]. That is to say, the higher the current density injected into the OLED layer, the faster the brightness of the OLED decreases. As shown in Fig. 6(b), when the brightness is 5000 cd/m^2, the initial current density of ITO-OLED, AgNW-OLED and AgNW@TiO_2-OLED is 12.6 mA/cm^2, 7.1 mA/cm^2, and 7.4 mA/cm^2, respectively. It is worth mentioning that the flexible OLED using AgNW-based anode has a longer life than ITO-OLED. The lifetime of AgNW-OLED and AgNW@TiO_2-OLED are 1.1 and 1.8 times longer than that of ITO-OLED.

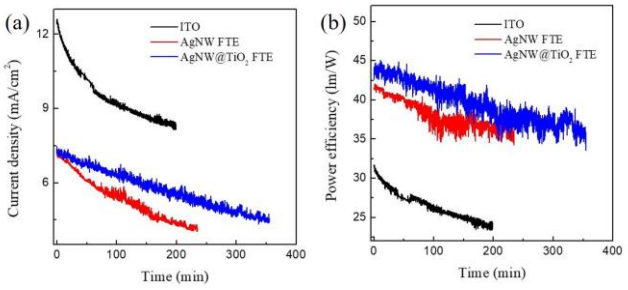

Fig. 6. (a) Variation of current density as a function of time, (b) variation of power efficiency as a function of time

We further characterized the morphologies of AgNW network and AgNW@TiO_2 network after testing lifetime, as shown in Fig. 7(a) and (b). It is obviously observed that the pristine AgNW network broken while the AgNW@TiO_2 remained network intact. These results suggest that the TiO_2 shell can effectively protect the AgNWs from the damage of Joule heat when OLED worked, and thus improving the lifetime.

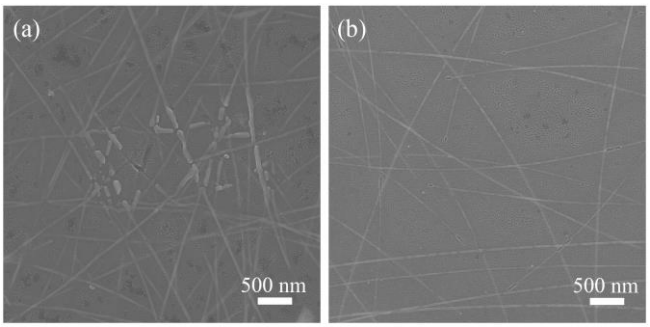

Fig. 7. Microstructure of FTEs after testing lifetime, (a) AgNW FTE, (b) AgNW@TiO_2 FTE

IV. Conclusion

In this paper, a long lifetime flexible OLED was prepared by AgNW@TiO_2 FTE. For the novel FTE, AgNW network was protected by uniform and conformal TiO_2 shell with thickness of 2-5 nm, which was prepared by facile and cost-effective solution-processed sol-gel method. The TiO_2 shell can significantly improve the stability of AgNW network under current stress, while it has negligible influence on transmission and can slightly increase conductivity. After embedding the conductive network into the polymer substrate, the FTEs with smooth surface were prepared. OLEDs were prepared by spin coating and evaporation techniques on ITO electrode, AgNW FTE, and AgNW@TiO_2 FTE. Based on the test results, the lifetime of ITO-OLED, AgNW-OLED, and AgNW@TiO_2-OLED are 200 min, 235 min, and 355 min, respectively. Compared with industrial OLED on ITO electrode, at the same voltage, the current density of OLED based on AgNW electrode is several times lower, thus, replacing ITO with AgNWs can improve the light-emitting efficiency of OLED and extend the lifetime of devices. However, because of Joule heat, the AgNWs were unstable under continuous current stress, shorten the lifetime of devices. After coating TiO_2 protective shell on AgNW network, the AgNW@TiO_2-OLED can work steadily, resulting long lifetime.

Acknowledgment

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