Transparent conductive PVP/AgNWs films for flexible organic light emitting diodes by spraying method[*]

HU Jun-tao (胡俊涛)**, **MEI Wen-juan** (梅文娟)**, **YE Kang-li** (叶康利)**, **WEI Qing-qing** (卫庆庆)**, and **HU Sheng** (胡晟)

National Engineering Laboratory for Special Display Technology, Key Laboratory on Special Display Technology of Ministry of Education in China, Provincial and Ministry Joint State Key Laboratory on Advanced Display Technology, Academy of Photoelectric Technology, Hefei University of Technology, Hefei 230009, China

In this study, a simple spraying method is used to prepare the transparent conductive films (TCFs) based on Ag nanowires (AgNWs). Polyvinylpyrrolidone (PVP) is introduced to modify the interface of substrate. The transmittance and bending performance are improved by optimizing the number of spraying times and the solution concentration and controlling the annealing time. The spraying times of 20, the concentration of 2 mg/mL and the annealing time of 10 min are chosen to fabricate the PVP/AgNWs films. The transmittance of PVP/AgNWs films is 53.4%—67.9% at 380—780 nm, and the sheet resistance is 30 $\Omega/\square$ which is equivalent to that of commercial indium tin oxide (ITO). During cyclic bending tests to 500 cycles with bending radius of 5 mm, the changes of resistivity are negligible. The performance of PVP/AgNW transparent electrodes has little change after being exposed to the normal environment for 1 000 h. The adhesion to polymeric substrate and the ability to endure bending stress in AgNWs network films are both significantly improved by introducing PVP. Spraying method makes AgNWs form a stratified structure on large-area polymer substrates, and the vacuum annealing method is used to weld the AgNWs together at junctions and substrates, which can improve the electrical conductivity. The experimental results indicate that PVP/AgNW transparent electrodes can be used as transparent conductive electrodes in flexible organic light emitting diodes (OLEDs).

Optoelectronic devices, including organic light emitting devices, graphic display, solar cells and the touch pane, require films used as the anode with high light transmittance and electrical conductivity[1-3]. To date, indium tin oxide (ITO), which has high transparency and low sheet resistance, is commonly used as the transparent electrode[4,5]. However, some problems, including the limited supply of indium, lack of flexibility and the complicated fabrication process, make ITO electrodes unsuitable for the use in flexible organic light emitting diodes (OLEDs)[6-9]. Recently, Ag nanowires (AgNWs) have attracted much research interest as an alternative of ITO due to their straightforward fabrication, high conductivity, mechanical ductility, as well as high corrosion stability[10-13].

However, AgNWs also have some disadvantage, such as the mechanical fracture under large bending, production of large area of the electrode, the weak storing for long time. Cheong et al[14] investigated the fabrication of transparent electrodes with AgNWs prepared by Meyer rod coating, in which the sheet resistance is increased by 30% after only 100 bending cycles. As it reported, the sheet resistance of the AgNWs transparent electrode fabricated by the mechanical press is increased by 60% after bending cycles[15]. Polyvinylpyrrolidone (PVP) is a kind of water-soluble polymers, as an excellent dispersant, and it was used by many researchers[16,17].

In this paper, in order to improve the bending performance, we demonstrate the transparent conductive films (TCFs) based on polyvinylpyrrolidone (PVP) and AgNWs on a flexible substrate by spraying method. By introducing PVP to modify the interface of substrate, the PVP/AgNWs films have the same high flexible and low sheet resistance (R_s) after bending cycles. Then thermal annealing is applied to weld the AgNWs together at junctions. We find that the combination of PVP and thermal annealing results in the mechanical and electrical stability. In addition, we successfully fabricate a flexible OLED using the prepared PVP/AgNWs electrodes.

All chemicals used in the experiment were analytic reagent. The AgNW suspension solution was provided by Nanjing XFNano Materials Tech Co., Ltd. AgNWs have

the mean diameter of about 40 nm and the mean length of about 1 μm. MoO_3 (99% purity), N,N-biphenyl-N,N-bis(1-naphenyl)-[1,1-biphenyl]-4,4-diamine (NPB, 99% purity), tris-(8-hydroxyquinoline) aluminium (Alq_3, 99% purity) and LiF (99% purity) were provided by Luminescence Technology Corp.

The electrical resistance was measured at room temperature by the four-point probe method. The optical transmittance spectrum at the range of 380—780 nm was measured using an ultraviolet (UV) spectrophotometer. The structure of the AgNWs on the substrate was observed using scanning electron microscopy (SEM). The surface coverage was investigated by an optical microscope (OM). The current density-voltage (*J-V*) characteristics of the OLEDs were measured by a Keithley 2400 source measure unit.

The substrates were firstly ultrasonic cleaned successively in acetone, ethanol and deionized water with each time of 15 min. The moisture was thoroughly removed by N_2 gas flow. To ensure the complete removal of all remaining water, the substrates were heated on a hot plate for 10 min at 100 °C.

On the other hand, 1 mL AgNW suspension solution with a concentration of 25 mg/mL was diluted by anhydrous ethanol to form the final solutions with four concentrations of 0.5 mg/mL, 1 mg/mL, 1.5 mg/mL and 2 mg/mL. Then PVP film was spin-coated onto substrate for 40 s with spinning speed of 4 000 r/min. After that, four AgNW suspension solutions with different concentrations were sprayed on PVP. The fabrication process of PVP/AgNWs transparent electrode is shown in Fig.1. Thermal annealing was done under a vacuum of 1.0×10^{-2} Pa.
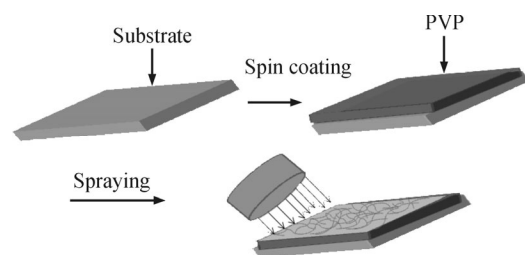

Fig.1 Schematic diagram of the process for constructing the PVP/AgNWs TCFs

The structure fabricated in this study as following, 10 nm-thick MoO_3 layer as the buffer layer, 40 nm-thick NPB as the hole transport layer, 60 nm-thick Alq_3 as green light emitting layer, and 1 nm-thick LiF capped with a 100 nm-thick Al cathode. High purity source materials of MoO_3, NPB, Alq_3, LiF and Al were successively evaporated on PVP/AgNWs anode or AgNWs anode prepared above under a vacuum of 2.0×10^{-6} Pa.

The influence of the number of sprayed times on the whole structure transmittance was firstly studied. Fig.2 shows the transmittance spectra of AgNWs films with different concentrations and different sprayed times on

photopolymer flexible substrate. It can be seen that when the numbers of sprayed times are 10 or 20, transmittance spectra of the four AgNWs films with concentrations of 0.5 mg/mL, 1 mg/mL, 1.5 mg/mL and 2 mg/mL are very close, and the transmittance spectrum of AgNWs film with high concentration of 2 mg/mL is slightly lower. When the numbers of sprayed times are 30, 40 and 50, transmittance spectra of the AgNWs films with high concentrations are obviously lower. It shows that the less number of sprayed times means the higher transmittance and the worse conductive ability. The effect of the number of spraying times on electrical performance is studied as shown in Tab.1. Samples with higher transparency typically show lower electrical conductivity. Low electrical conductivity is produced in AgNWs polymer composite structure, which is related to a low surface coverage of AgNWs. It is concluded that the AgNWs film with the number of sprayed times of 20 has high transmittance of 53%—69% at 380—780 nm as shown in Fig.2(b) and high conductivity of 30—192 Ω/□ as shown in Tab.1.
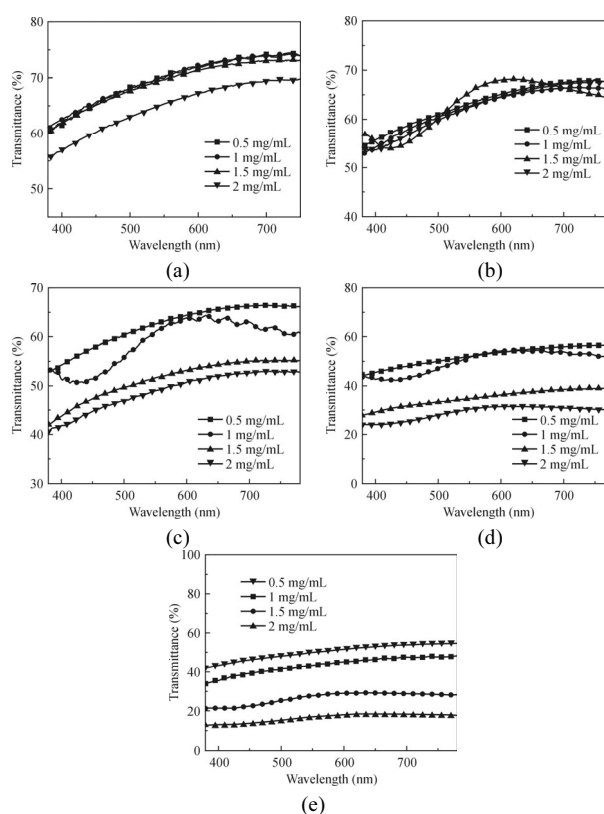

Fig.2 The transmittance spectra of AgNWs films of different concentrations on photopolymer flexible substrate prepared with different spraying times of (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50

Fig.3 shows the top surface images of the AgNWs films with the number of sprayed times of 20 and four concentrations on the substrate via an optical microscope (OM). It can be seen from Fig.3 that the AgNW networks become sparser on the substrate as the concentration decreases. 0.5 mg/mL is the smallest concentration, so

the corresponding AgNWs film has the lowest coverage. The AgNWs film with concentration of suspension solution of 2 mg/mL has the highest coverage. The surface resistance and transmittance are taken into account. Finally, the spraying time of 20 and the AgNWs suspension concentration of 2 mg/mL are indentified as the most suitable selection for use in flexible OLEDs, in which the transmittance is 53.4%—67.9% at 380—780 nm, and the sheet resistance is 30 Ω/□.

Tab.1 Sheet resistance (Ω/□) of AgNWs films with different conditions and different spraying times

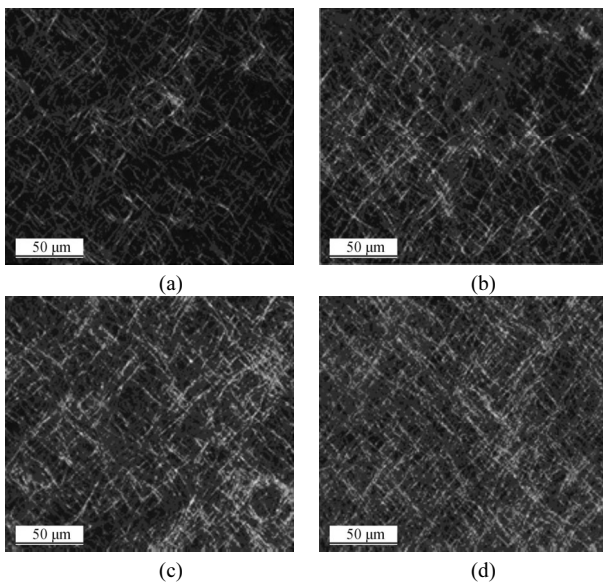| Spraying times	Concentration (mg/mL)			
	0.5	1	1.5	2
10	305	236	185	80
20	192	124	76	30
30	136	93	45	11
40	56	37	16	5
50	26	15	7	4

(a)   (b)

(c)   (d)

Fig.3 OM images of the AgNWs films with the sprayed time of 20 on polymer substrates with different concentrations of AgNWs suspension solutions of (a) 0.5 mg/mL, (b) 1 mg/mL, (c) 1.5 mg/mL and (d) 2 mg/mL

It's reported that melting starts from surface of AgNWs after annealing. The analyses of PVP/AgNWs film after different thermal annealing time at approximately 100 °C were done by SEM. Sample annealing was performed in oven with vacuum of 1.0×10^{-2} Pa at 100 °C for different time of 5 min, 10 min, 15 min and 20 min. Fig.4(a) shows the SEM image of original sample. Fig.4(b)—(e) show the SEM images of samples after thermal annealing at 100 °C for 5 min, 10 min, 15 min and 20 min, respectively. Fig.4(f) shows the measured transmittance spectra of PVP/AgNWs films after differ-

ent annealing time. It can be seen from Fig.4(b)—(e) that the junction of AgNWs has different degree of adhesion after different annealing time. When the annealing time is 5 min, junctions change slightly. When the annealing time goes up to 10 min, junctions have very good adhesion, and AgNWs still keep a good linear. Continue to anneal, linear structure becomes deformation. It is concluded that when annealing time less than 10 min, thermal annealing has no damage to one-dimensional linear structure of AgNWs. Form Fig.4(f), it can be seen that the transmittance spectra of the PVP/AgNWs films with thermal annealing time of 0 min, 5min and 10 min overlap together, and the transmittance of PVP/AgNWs films becomes smaller with the further increase of annealing time.

(a)   (b)
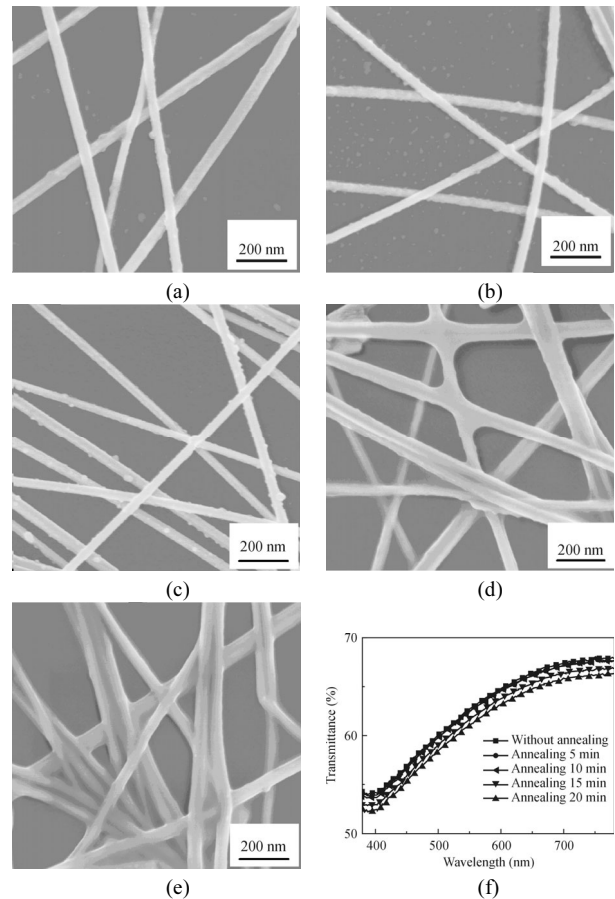
(c)   (d)

(e)   (f)

Fig.4 The SEM images of AgNWs junctions (a) before and after annealing for (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min; (f) The optical transmittance spectra after different annealing time

Fig.5(a) shows the resistance of PVP/AgNWs films after different annealing time. It can be seen that when thermal annealing time goes up from 0 min to 10 min, the sheet resistance is greatly decreased resulting from the reduced junction resistance. The sheet resistance of the PVP/AgNWs film is decreased by 0.5 Ω/□ after the vacuum annealing for 10 min. So it is concluded that the optimized annealing time is 10 min, which improves the

electrical conductivity and has no effect on transmittance.

Fig.5(b) shows the sheet resistance as a function of the number of bending cycles with bending radius of 5 mm for PVP/AgNWs films and AgNWs films. The resistance of the AgNWs films is increased by 20 $\Omega/\square$ rapidly after 500 bending cycles, which indicates that the inter-nanowire junctions are unstable and the mechanical adhesion with the substrate is poor. The sheet resistance of the PVP/AgNWs films is much more stable. The reason is that AgNWs are parceled immediately by PVP when ions are sprayed onto the substrate, and then the PVP enhances the adhesion of the AgNW networks to the substrate due to its water absorbability, so the flexibility is greatly enhanced.
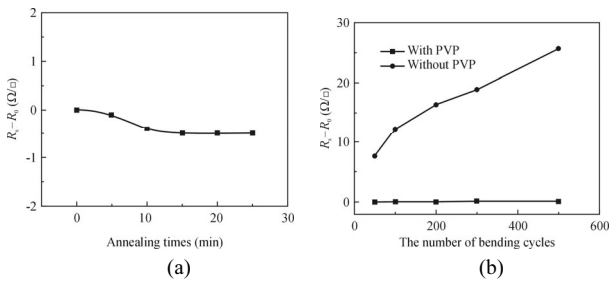

Fig.5 The change of sheet resistance with initial value R_0=30 $\Omega/\square$ as function of (a) annealing time and (b) the number of bending cycles for PVP/AgNWs and AgNWs TCFs

The adhesion between PVP/AgNWs films and polymer substrates as well as between AgNWs films and polymer substrates is investigated as shown in Fig.6. These films were immersed in a sonication bath filled with two solutions of deionized water and alcohol. The AgNWs films become non-conductive after being immersed into two solutions because some AgNWs are separated from the polymer substrates. After 30 s, the AgNWs are completely separated from the polymer substrates. But the sheet resistance of the PVP/AgNWs films is increased by only 15 $\Omega/\square$ after 180 s, and the PVP/AgNWs films show the enhanced chemical stabilities in these two solutions. The AgNWs with PVP exhibit slightly better stability than that of the AgNWs without PVP, which is consistent with the ultrasonic test. It confirms our conjecture that the insertion of PVP between AgNWs and polymeric substrate enhances the chemical and mechanical stabilities of the AgNW films.

Furthermore, we fabricate the OLEDs with PVP/AgNWs and AgNWs TCFs. The structure is as follows, anode/MoO$_3$/NPB/Alq$_3$/LiF/Al, where anode refers to PVP/AgNWs anode or AgNWs anode. Experiment results prove that the PVP/AgNWs transparent electrodes prepared by spraying method can be used in flexible OLEDs. Fig.7 shows the *J-V* characteristics of the PVP/AgNWs based OLED and AgNWs based OLED. The current density of the PVP/AgNWs based OLED is larger than AgNWs based OLED. The current density of

PVP/AgNWs based OLED reaches 568 mA/cm^2, while that of AgNWs based OLED is 334 mA/cm^2 as shown in Fig.7. It's clear that the performance of PVP/AgNWs based OLED is better than that of AgNWs based OLED. The surface of AgNWs without modification directly deposited on PVP is extremely rough, which results in the poor luminous performance of OLEDs. If the stacking AgNWs networks are modified by other conductive materials, the efficiency of diodes can be improved. And the related work will be studied in future.
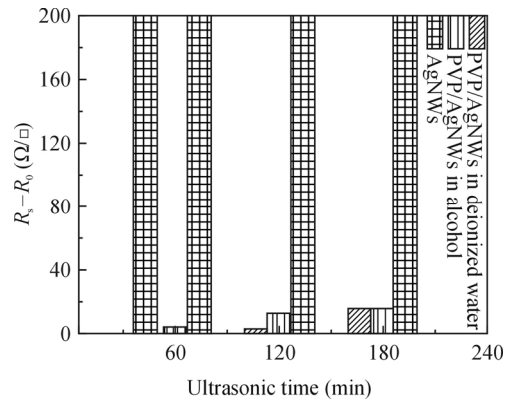

Fig.6 The change of sheet resistance with initial value R_0=30 $\Omega/\square$ for AgNWs films and PVP/AgNWs films after ultrasonic in deionized water and alcohol
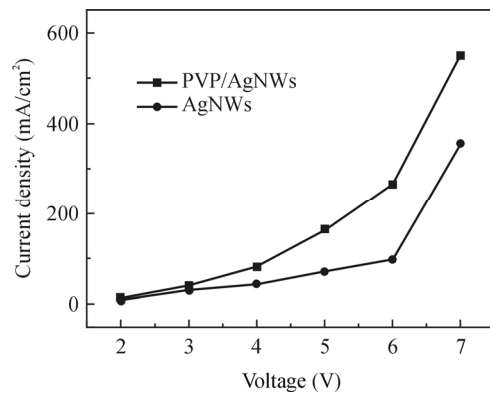

Fig.7 *J-V* characteristics of PVP/AgNWs based OLED and AgNWs based OLED

Finally, the sheet resistance of the transparent conductive PVP/AgNWs films is measured after being placed in the atmospheric environment for 1 000 h. The sheet resistance is only increased to 36 $\Omega/\square$. This proves once again that the transparent conductive PVP/AgNWs films have stable performance as a result of the PVP colloid protection and multilayer spraying technology.

In conclusion, the stability of PVP/AgNWs film on flexible photopolymer substrate is demonstrated by optimizing the number of spraying times, the solution concentration and the vacuum annealing time. The spraying time of 20, the concentration of 2 mg/mL and annealing time of 10 min are chosen to fabricate the PVP/AgNWs films. The transmittance of PVP/AgNWs films is 53.4%—67.9% at 380—780 nm, and the sheet resistance is 30 $\Omega/\square$

which is equivalent to that of commercial ITO. During cyclic bending tests to 500 cycles with bending radius of 5 mm, the change of resistivity is negligible. The PVP/AgNWs films exhibit stability after being exposed in the atmospheric environment. PVP significantly improves its adhesion to polymeric substrate and the ability to endure bending stress, and then the vacuum annealing method is used to weld the AgNWs together at junctions and substrates. This preparation method is easier to implement the pattern of electrodes for massive production. Finally, we successfully fabricate the flexible OLEDs on the welded AgNWs networks. This demonstrates that the film manufacturing processes developed here can be used in flexible OLEDs.

References

[1]   B. Meng, W. Tang, Z. H. Too, X. S. Zhang, M. D. Han, W. Liu and H. X. Zhang, Energy & Environmental Science **6**, 3235 (2013).

[2]   C. Y. Xiang, W. Koo, F. So, H. Sasabe and J. Kido, Light-Science & Applications **2**, e74 (2013).

[3]   Y. F. Liu, J. Feng, Y. F. Zhang, H. F. Cui, D. Yin, Y. G. Bi, J. F. Song, Q. D. Chen and H. B. Sun, Organic Electronics **15**, 478 (2013).

[4]   S. Takamatsu, T. Takahata, K. Matsumoto and I. Shimoyama, Journal of Micromechanics and Microengineering **21**, 75 (2011).

[5]   Ross E. Triambulo, Hahn-Gil Cheong and Jin-Woo Park, Organic Electronics **15**, 2685 (2014).

[6]   Hai-Feng Cui, Yi-Fan Zhang and Chuan-Nan Li, Optical Engineering **53**, 077102 (2014).

[7]   LI Xiao-yun, HU Wen-zheng and LIU Guo-rui, Journal of Optoelectronics·Laser **25**, 1855 (2014). (in Chinese)

[8]   W. Gaynor, G. F. Burkhard, M. D. McGehee and P. Peumans, Advanced Materials **23**, 2905 (2011).

[9]   M. L. Zhang, F. H. Zhang, W. Zhang and J. Huang, Journal of Optoelectronics·Laser **25**, 425 (2014). (in Chinese)

[10]   F. Xu and Y. Zhu, Advanced Materials **24**, 5117 (2012).

[11]   LUO Yang, LI Tianjiao and DUAN Yu, Journal of Optoelectronics·Laser **25**, 840 (2014). (in Chinese)

[12]   T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B. H. Hong, J.-H. Ahn and T.-W. Lee, Nature Photonics **6**, 105 (2012).

[13]   M. Kavitha, M. R. Pararida, E. Prasad, C. Vijayyan and P. C. Deshmukh, Macromolecular Chemistry and Physics, **210**, 1310 (2009).

[14]   Hahn-Gil Cheong, Ross. E. Triambulo, Gun-Hwan Lee, In-Sook Yi and Jin-Woo Park, ACS Applied Materials & Interfaces **6**, 7846 (2014).

[15]   Lu Li, Zhibin Yu, Weili Hu, Chia-hao Chang, Qi Chen and Qibing Pei, Advanced Materials **23**, 5563 (2011).

[16]   Hatice Kaplan and Ali Guner, Journal of Applied Polymer Science **78**, 994 (2000).

[17]   Stéphanie Vial, Isabel Pastoriza-Santos, Jorge Pérez-Juste and Luis M Liz-Marzan, Langmuir **23**, 4606 (2007).