Spraying preparation of flexible AgNWs-PEDOT:PSS/PET transparent conductive films with high bendability and low optical haze

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The AgNWs-PEDOT:PSS/PET transparent conductive films with high bendability and low optical haze were prepared by a facile spraying process combining with mechanical press treatment. When the ratio of PEDOT:PSS solution vs. AgNWs is 0.2, the conductive film has excellent properties with a sheet resistance of 80.3 Ω/sq, transmittance of 87.4%, a haze of 5.5% and a surface roughness of 25.6 nm. After being mechanically pressed under 4 MPa pressure, the film possesses a sheet resistance of 39.5 Ω/sq, transmittance of 87.4% and haze of 4.3%. The adhesion and bendability are also greatly enhanced with only 15.6% increase of sheet resistance after 20,000 bending cycles.

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1. Introduction

Conductive films with high transmittance is a vital part for many photoelectric devices such as touch screen, organic light-emitting diode, solar cells [1-4]. The most popular transparent conductive film is ITO [5]. However, the ITO film would be replaced due to its high cost and fragility [6,7]. Recently, many researchers have found that the AgNWs film is a promising candidate for the flexible transparent conductive films owing to its excellent physical properties and mechanical behavior [8,9]. Furthermore, the AgNWs transparent conductive film can be prepared at a lower temperature compared with ITO film to reduce the deformation of plastic substrates [10,11].

Even so, there are still some challenges hindering the application of the AgNWs film for large-scale devices [12,13]. There into, the adhesion between the AgNWs and substrate is a critical factor that needs to be further enhanced. Without the strong adhesion, the AgNWs would fall off from the substrate when bended and cause the sheet resistance increase. How to improve the adhesion force becomes an important issue. In the past works, some measures have been reported. For example, Take hiro et al. fabricated the AgNWs transparent electrodes by the mechanical press under 25 MPa at room temperature with a 19% increase of sheet resistance after 1000 bending cycles [14]. In order to further enhance the adhesion, Cui's group applied Teflon as encapsulating material to stabilize AgNWs networks on the flexible substrate [15]. Other utilizing polymers as both substrate and binder such as polydimethylsiloxane(PDMS) [16], polyacrylate [17], polyurethane (PU) [18], poly(methyl methacrylate) (PMMA) [19], poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) [20-23], polyimide (PI) [24], polycarbonate (PC) [25], and polyvinyl alcohol (PVA) [26] have joined into the family of AgNWs hybrid electrodes. This method is proved to be effective for improving the adhesion, just as Ghosh et al found that their prepared AgNWs/PI conductive film has little change for the sheet resistance with 3.7% increase after 1000 bending cycle [24]. What will be the results if combing the mechanical press with polymer encapsulating?

Meanwhile, the optical haze of the film is also an important parameter as the adhesion, which greatly influences the transmittance of the film and their application in touch screen or solar cells, etc. [27,28]. While the haze can be affected by the film composition and surface roughness when the film was pressed or coated by polymers.

Therefore, in this work, the AgNWs-PEDOT: PSS/PET conductive films were prepared by using a facile spraying process followed by the mechanical press method, and the influence the PEDOT:PSS content and press treatment on the optical, electrical and mechanical properties were investigated.

2. Experimental

The AgNWs suspension with a concentration of 10 mg/mL was bought from Ji'nan Kexin New Materials Technology Co. Ltd. of China, the diameter of the AgNWs is approximately 40 nm, and the length is 20~30 μm. The PEDOT:PSS solution with a concentration of 0.72 mg/mL was bought from Cold-stone Tech Co., Ltd of China).

Firstly, the AgNWs suspension was diluted to a concentration of 0.8 mg/mL and supersonic vibrated for 30s. A PET substrate was cut into 8cm×8cm squares, then ultrasonic washed in deionized water, acetone, and alcohol for 5 min respectively. Then, 4.5 mL AgNWs suspension was mixed with the PEDOT:PSS solution of 0ml, 0.5 ml, 1 ml, 1.5 ml and 2 ml. The mass ratio of the PEDOT:PSS versus AgNWs is 0, 0.1, 0.2, 0.3 and 0.4. Secondly, the mixed solution was sprayed on the PET substrate by the airbrush to form the AgNWs /PEDOT:PSS conductive film. Thirdly, the conductive films were carefully dried in an oven at 80 ^{o}C for 10 min to remove the organic solvent. At Last, to enhance the adhesion between the films with the substrate, mechanical press treatment was applied uniformly on the films by a tablet machine.

The optical transmittance spectra were investigated by a Beijing PGeneral TU-1900 ultraviolet-visible spectroscopy (UV-vis) spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) at the range of 350–900 nm with a blank PET substrate as the reference. The corresponding sheet resistance was measured using ST2258c four-point probe technique (Suzhou Jingge Electronics Co. Ltd). The haze of the conductive films was investigated by a WGW photoelectric haze meter (Shanghai instrument physical optics instrument Co., Ltd). The composition analysis was conducted by ESCALABMarkII X-ray photoelectronmeter (XPS, VG, UK). An Al Ka X-ray source ($h\gamma$ = 1486.6 eV) was used for the excitation of electrons. The surface morphology of the films was observed by a JEOL JSM-7001 field emission scanning electron microscope (SEM; JEOL Ltd., Tokyo, Japan). The surface roughness was measured by using a MicroNano D3000 atomic force microscopy (AFM, Shanghai Zhuolun MicroNano Instrument Co., Ltd., China). The bending performance for the fabricated AgNWs-PET films was determined by measuring the sheet resistance change of the films with the bending cycles using a reciprocation motion machine.

3. Results and discussion

Fig. 1 shows the XPS spectra of the AgNWs/PET and AgNWs-PEDOT:PSS /PET, respectively. From the spectra of the Ag*3d*, the binding energy of the $3d_{5/2}$ and $3d_{3/2}$ is 367.7 eV and 373.7 eV respectively, the same as the standard Ag bonding energy. It indicates that the PEDOT:PSS does not influence the surface state of the AgNWs. C*1s* spectra have three binding energy, 284.6 eV, 286.0 eV, 288.6 eV, representing the bond C-C, C=C, C=O, respectively, which is the natural bond of PET and PEDOT. Meanwhile, the spectra of O*1s* and S*2p* indicate the existence of the PEDOT:PSS, which could not change the state of AgNWs on the PET substrate but could form the hydrogen bond and electrostatic adherence to improve the stability and the bond strength of the AgNWs with PET substrate.

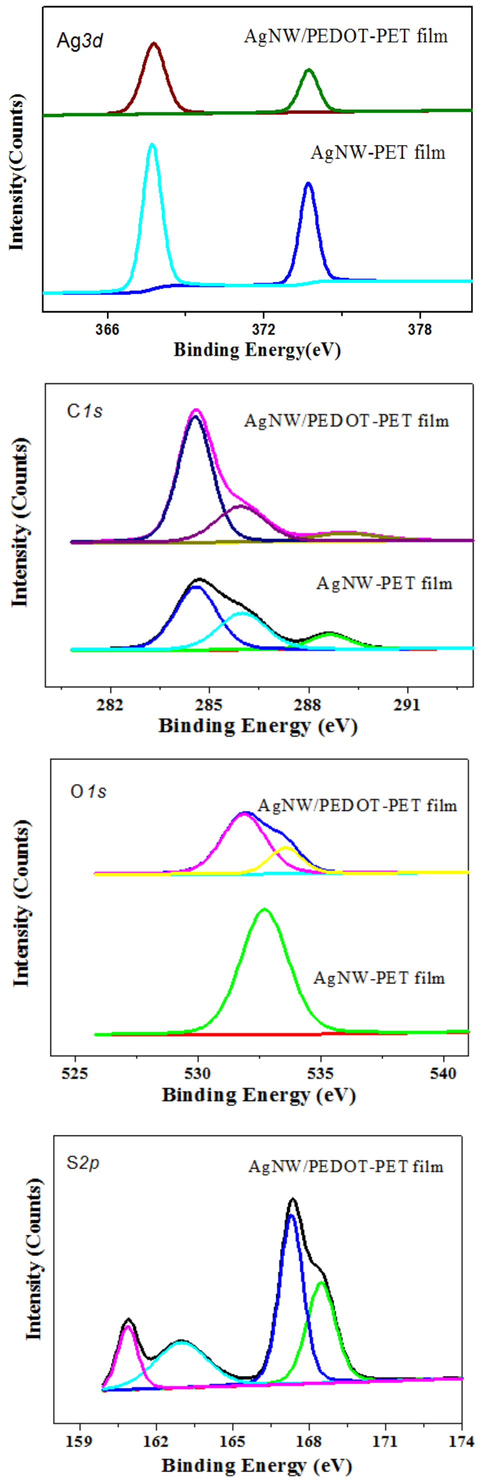

Fig. 1. XPS spectra of AgNWs/PEDOT:PSS film compared with AgNWs/PET film

To investigate the influence of the PPEDOT:PSS content on the properties of the AgNWs/PEDOT:PSS conductive films, the different ratios of PEDOT: PSS vs. AgNWs of 0.1, 0.2, 0.3 and 0.4 were chosen. Fig. 2 shows the SEM images of the AgNWs-PEDOT:PSS/PET conductive films with different PEDOT:PSS content. From Fig. 2 (a), only a part of AgNWs are coated by the

PEDOT:PSS and there is still a lot of space between the AgNWs. As the content of PEDOT:PSS increases gradually, the AgNWs can be encapsulated by the PEDOT:PSS. Meanwhile, the blank space in the AgNWs network can also be filled by the PEDOT:PSS as displayed in Fig 2 (b), which could increase the contact area and create an uniform surface. However, when the PEDOT:PSS content was increased to 0.3 or 0.4 (Fig. 2 (c), (d)), most of the AgNWs were covered by the PEDOT:PSS due to the excessive PEDOT:PSS, which may influence the transmittance of the conductive films.

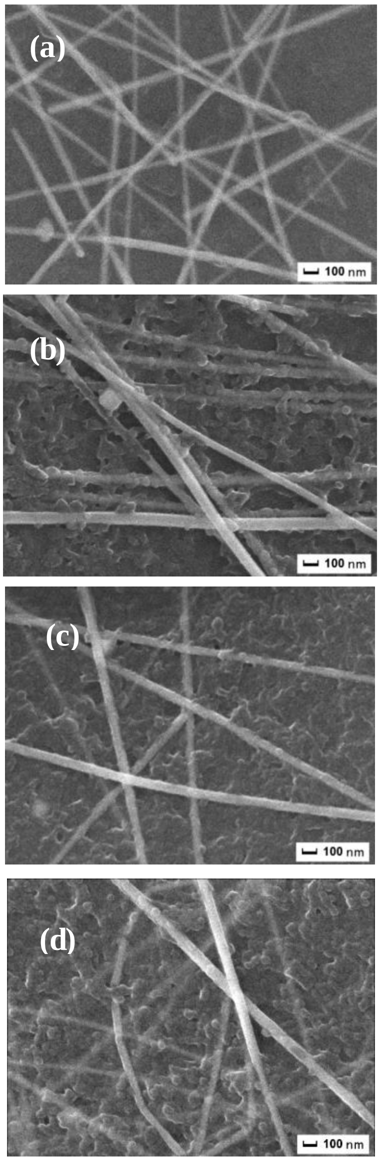

Fig. 2. SEM images of AgNWs/PEDOT:PSS films with different ratios of PEDOT:PSS vs. AgNWs, (a) 0.1; (b) 0.2; (c) 0.3 (d) 0.4

Fig. 3 (a) shows the change of transmittance, sheet resistance and optical haze of the AgNWs-PEDOT:PSS/PET conductive films with the different PEDOT:PSS content. It can be seen that with the increase of the PEDOT:PSS content, the transmittance of the conductive films decreases gradually. It is worth to note that a small quantity of PEDOT:PSS has little influence on the transmittance of the films, for example, when the ratio increases from 0 to 0.2, the transmittance of the conductive films just decreases from 88.69% to 87.4% at the wave length of 550 nm. But, when the ratio is increased to 0.4, the transmittance of the conductive films decreased to 83.4%. In addition, the sheet resistance of the film is also affected by the content of PEDOT:PSS. As displayed in Fig. 3(a), with the increase of the PEDOT:PSS, the sheet resistance of the AgNWs-PEDOT:PSS-PET conductive film decreases gradually. When the ratio of the PEDOT:PSS vs. AgNWs is increased from 0 to 0.4, the sheet resistance of the conductive film can decrease from 84.4 Ω/sq to 45.2 Ω/sq. The reason is that the PEDOT:PSS can also provide conductive path to enhance the conductivity of the film besides AgNWs [20]. While from the change trend of the haze, it can be seen that the haze of the film will increase gradually with the addition of PEDOT:PSS. By considering the transmittance, sheet resistance and haze of the films, the ratio of 0.2 is thought to be suitable for the AgNWs-PEDOT:PSS-PET conductive film.

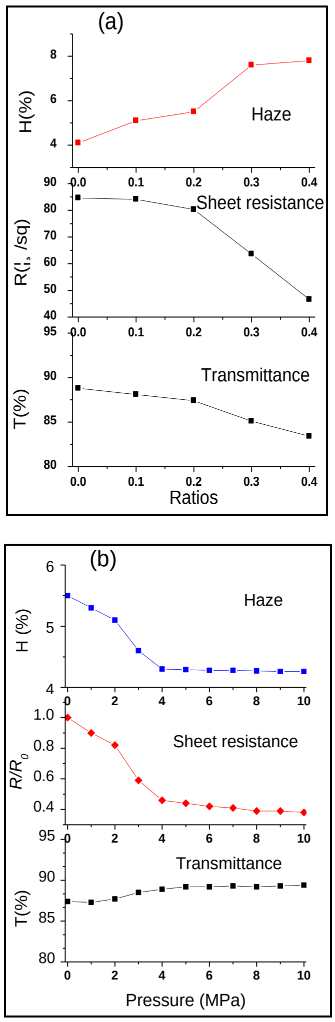

Fig. 3. The effects of the ratios of PEDOT:PSS vs. AgNWs(a) and pressures(b) on the haze, sheet resistance and transmittance of AgNWs-PEDOT:PSS/PET films

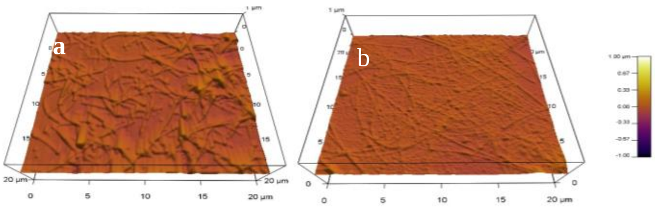

Fig. 4. AFM pictures of AgNWs/PEDOT:PSS film before (a) and after (b) press treatment under 4 Mpa

Fig. 3(b) shows the change of transmittance, sheet resistance and optical haze of the AgNWs -PEDOT:PSS/PET conductive film at the ratio of 0.2 with the different pressures by mechanical pressing. From Fig. 3(b), it can be seen that all three have been improved by mechanical pressing. The transmittance of the film shows a little increase with the rise of pressure, while the sheet resistance and the haze are declined greatly from 80.3 Ω/sq to 39.5 Ω/sq and 5.5% to 4.3% under the pressure of 4MPa. Meanwhile, according to the analysis of AFM shown in Fig. 4, the surface roughness of AgNWs-PEDOT:PSS/PET film before and after mechanical pressing at 4MPa was clearly decreased from 25.6 nm to 14.3 nm. From the above results, it can be deduced that the press treatment can make the surface of the conductive film more smooth, leading to less light scattering and lower haze.

Fig. 5(a) shows the adhesion test results of the AgNWs-PEDOT:PSS/PET conductive films before and after press treatment by 3M adhesive tape as our before reports [29]. The sheet resistance of the AgNWs-PEDOT:PSS/PET conductive film pressed with 4 MPa keeps stable with a little change of 8 Ω/sq after one time adhesion test, while the sheet resistance of the unpressed AgNWs/PEDOT:PSS conductive film increases by more than 1 times due to the peeling of AgNWs after adhesion test. Accordingly, the transmittance and haze of the AgNWs-PEDOT:PSS/PET film without press treatment have some change as well, but the pressed one remains very stable. Fig. 5 (b) is the sheet resistance change of the AgNWs-PEDOT:PSS/PET conductive films before and after press treatment under 4 MPa with the bending cycles. Compared with the unpressed film, the bendability of the pressed AgNWs-PEDOT:PSS/PET conductive film was greatly enhanced with nearly unchanged sheet resistance after 5000 bending cycles, only an increase by 15.6% after 20,000 bending cycles.

4. Conclusions

In this paper, the AgNWs-PEDOT:PSS/PET conductive films were prepared by combining spraying method and mechanical press process. When the ratio of PEDOT:PSS solution vs. AgNWs is 0.2, the AgNWs-PEDOT:PSS/PET conductive film has excellent properties with a sheet resistance of 39.5 Ω/sq, transmittance of 87.4%, haze of 4.3% and the surface roughness of 14.3 nm after the film was mechanically pressed under 4 MPa pressure, the adhesion and bendability were also greatly enhanced with 15.6% increase of sheet resistance after 20,000 bending cycles.

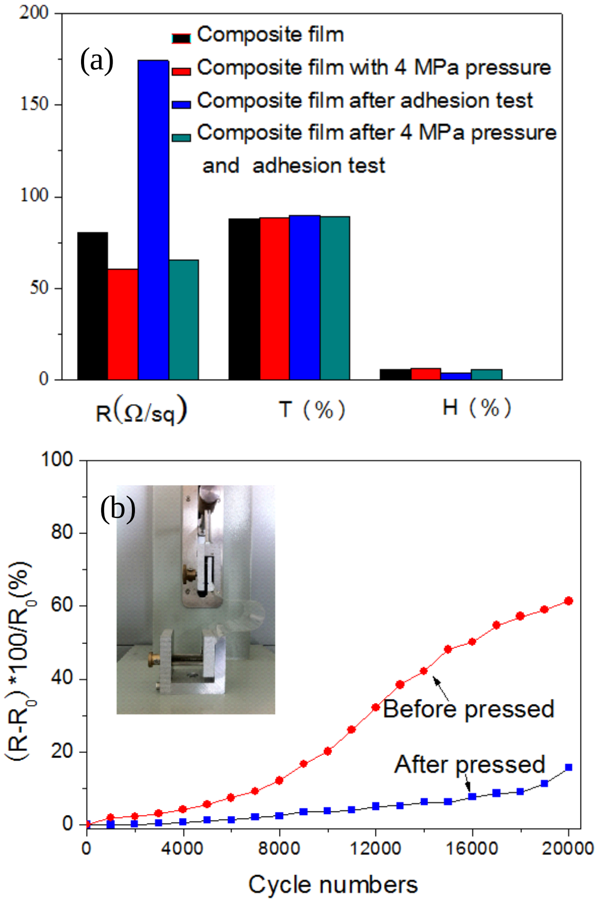

Fig. 5. The results of adhesion test (a) and the bendability test with bending cycles (b) for the AgNWs-PEDOT:PSS/PET conductive films before and after 4 MPa press treatment

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