High Performance Silver Nanowire based Transparent Electrodes Reinforced by Conductive Polymer Adhesive

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***Abstract*—Transparent conducting electrodes (TCEs) are an essential component for modern opto-electronic devices such as solar cells, organic light emitting diodes (OLEDs), liquid crystal displays (LCDs), and touch screen panels. However, traditional indium tin oxide (ITO) cannot meet the demand for the next generation highly flexible TCEs, and thus many novel alternative materials and technologies are blooming, such as super-aligned carbon nanotube, graphenes, conducting polymer and metal nanowire and so on. Among them, silver nanowires (Ag NWs) have been considered as one of the most promising technologies for TCEs, featured with superior electrical and optical properties. However, there are still two major challenges for Ag NWs-based TCEs technology to overcome. One is the poor mechanical interconnection between the Ag NWs conducting networks and transparent substrate, the other is the high contact resistance of the junctions among Ag NWs. Here we report a novel two-step electrostatic spraying process to fabricate Ag NWs TCEs composite with selectively coated conductive polymer, i.e. poly 3,4-ethylenedioxythiophene: polystyrenesulfonate (PEDOT:PSS). Additionally, we applied plasma treatment to the materials between two-step electrostatic spraying process, which rendered sintering of junctions between the Ag NWs at room temperature, and thus increasing the conductivity of the TCEs by at least three orders of magnitude. Results showed that by adjusting the electrostatic spraying process parameters, selective deposition can be achieved, i.e. the conductive polymer could tightly bound to the Ag NWs network. As compared to an even distribution of the coating layer in the whole area, selective coating rendered the negligible loss of transmittance (0.2% at most) and excellent adhesion to the substrate. Moreover, the composited TCEs exhibited 85.3% mean optical transmittance and 35.8 Ω/sq sheet resistance. Based on our results, we believe that this technology can be used for roll-to-roll preparation of silver nanowires (Ag NWs)-based TCEs.**

Keywords—Transparent electrodes, Silver nanowires (Ag NWs); Conductive polymer; Plasma treatment, Electrostatic spraying; Selective deposition component

I. INTRODUCTION

Transparent conducting electrodes (TCEs) have found more applications than ever in many fields. As an essential components in modern opto-electronic devices, TCEs are wildly used in various applications such as solar cells, organic light emitting diodes (OLEDs), liquid crystal displays (LCDs), and touch screen panels.[1] Currently, most TCEs are based on transparent conducting oxides (TCOs). Among them, indium tin oxide (ITO) is still the most common material due to its low sheet resistance and high optical transparency.

However, traditional indium tin oxide (ITO) cannot meet the growing demand for the next generation highly flexible TCEs owing to its own brittleness and high cost, and thus many new alternative materials and technologies are blooming, such as super-aligned carbon nanotubes, graphenes, conducting polymers and metal nanowires and so on.[2-5] Among them, silver nanowires (Ag NWs) have been considered as one of the most promising materials for fabricating novel TCEs due to its good reliability, recyclability and the excellent ability to adapt flexibility. The coating methods such as Mayer-rod, spin coating, air-spraying and so on are demonstrated to fabricate Ag NWs-based TCEs in associated research. [6-11] However, poor mechanical connection between the Ag NWs conducting networks and transparent substrates is one of the challenges ahead of Ag NWs based TCEs. In order to solve this problem, it is reported that conducting polymer, TCOs and some engineering resin could be used as adhesive for improving the connection.[12-14] The other challenge is the large contact resistance of the junctions between Ag NWs, and thus heat-treatment, high intensity pulsed light, and hot-pressing techniques were involved. [15,17-19] Here we report a two-step electrostatic spraying process to fabricate Ag NWs TCEs composite with selectively coated conductive polymer, which can overcome the as-mentioned drawbacks and prepare Ag NWs-based composite TCEs with high optical and electrical performance.

II. EXPERIMENTAL PROCEDURE

A. Materials

20 mg/mL Ag NWs suspension (purchased from Nanjing XFNANO Materials Tech Co. Ltd.; diameter: 60-100 nm; length: 10 - 20 μm) was diluted into 1 mg/mL with ethanol. DMSO was added to the PEDOT:PSS solution by a 15% weight ratio (Clevios P, Heraeus Clevios GmbH.), and then the

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doped PEDOT:PSS mixture was filtered using 0.45 mm poly(vinylidene difluoride) syringe filters. The PEDOT:PSS mixture was diluted by 50 vol% in ethanol to reduce viscosity and surface tension. The above-mentioned ethanol and DMSO was purchased from Sinopharm Chemical Reagent Co., Ltd. The PET substrates were obtained from Ningbo Hughstar Advanced Material Technology Co., Ltd.

B. Measurements

The sheet resistances of the TCEs were measured by a 4-point probe system (Mitsubishi MCP-T610). All the field-emission scanning electron microscopy (FE-SEM) images were taken on a HITACH S4800, Japan. Optical transmission spectra of the Ag NWs films were recorded using a UV/VIS/NIR spectrophotometer (TU-1810PC), and the reference spectra were evaluated from the bare PET substrates. The plasma treatment was achieved in the plasma washing machine from Chengdu Mingheng Science & Technology Development Co. Ltd. (PDC-MG). The radio-frequency power (13.56 MHz) was 0 to 150W.

C. Transparent electrodes fabrication

The Ag NWs layer and the conductive polymer adhesive layer were prepared on a transparent substrate using the electrostatic spraying technique. The experimental setup includes a stainless steel nozzle (inner diameter: 0.6 mm, outer diameter: 0.8 mm) and a static electric field. A syringe pump was used to control the feeding rate of 1 mg/mL Ag NWs suspension. The form factors were crucial for obtaining smaller droplet size and even distribution of the coating layer. In this study, the liquid flow rate of all electrostatic spray conditions were maintained at a 0.4 mL/min (Ag NWs suspension) and 0.04 mL/min (PEDOT:PSS mixture) respectively, 5 cm distance was kept between the nozzle and the substrate. As shown in Fig.1, The nozzle was used as the anode and the stainless steel plate below was used as the cathode. The potential applied in nozzle was +16 kV and +20 kV in the Ag NWs solution and the PEDOT:PSS solution respectively. In the meantime, potential applied in the cathode was -1 kV in these depositions. In addition, during the selectively deposition of the latter, the prepared Ag NWs coating below was used as the cathode, and the other parameters are the same.

For the preparation process, firstly, the PET substrates were purged in a plasma chamber (PDC-MG, treatment time: 5min); secondly, the Ag NWs deposition was conducted by electrostatic spraying method (deposition time: 3-10min). Since ethanol was highly volatile, no heating step was required after this step. Then the plasma treatment were applied to the deposited Ag NWs layer using a plasma chamber (treatment atmosphere: air, treatment time: 15 min).Thirdly, the PEDOT:PSS mixture was deposited on the fresh Ag NWs layer. The deposition time was 30 min and 5 min respectively. Finally, Ag NWs–PEDOT:PSS composite TCEs were heated at 60℃ to accelerate the evaporation of the solvent.

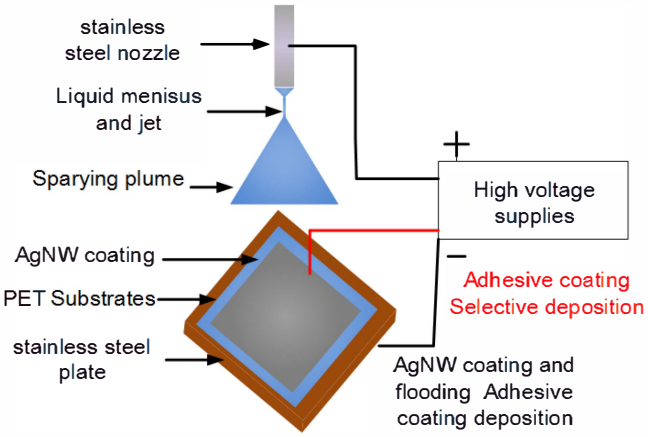

Fig.1 Schematic illustration of electrostatic spraying method method for Ag NWs coatings and conductive polymer adhesive coatings

III. RESULTS AND DISCUSSIONS

A. Characterization of TCEs

SEM images indicate that the Ag NWs on the substrates were uniformly distributed to form effective conducting network, which showed negligible difference in Ag NWs packing density (Fig. 2(a)-(b)), and the 2D percolation structure remained its integrity after the pre-deposited Ag NWs was buried by the PEDOT:PSS coating (Fig. 2(c)). Fig. 2(d) shows that the Ag NWs-PEDOT:PSS composite film was transparent. The sheet resistance and optical transmittance were examined by testing a series of TCEs prepared via the methods. In our work, the TCEs films of showed 84.9% transparency and 30.9 Ω sq^{-1} sheet resistances. Various electrical and optical properties of Ag NWs-PEDOT:PSS composite TCEs with different Ag NWs weight densities are shown in table 1.

Table 1 Comparison of the electrical and optical properties of Ag NWs-PEDOT:PSS composite TCEs with different Ag NWs weight densities deposited on the PET substrate

Ag NWs weight densities(mg/m^2)	$T_{550\ nm}$ (%)	Sheet resistance (Ω/sq)
140	84.9	30.9
148	82.8	22.7
167	76.4	13.5
174	73.1	8.5
180	70.8	6.7

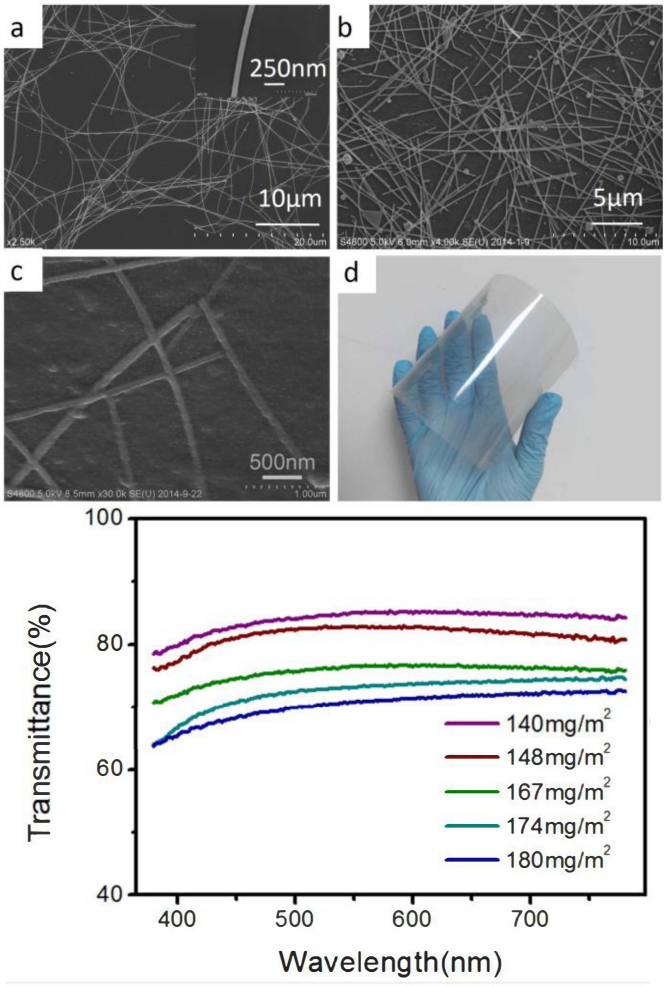

Fig. 2(a) SEM image of the Ag NWs before the electrostatic spraying. Inset shows the diameter of the Ag NWs (diameter ~ 60nm); (b) SEM image of the Ag NWs network fabricated by the electrostatic spraying; (c) SEM image of the Ag NWs–PEDOT:PSS composite film deposited on a PET substrate; (d) Photograph of the Ag NWs–PEDOT:PSS composite film deposited on a PET substrate; the mean optical transmittance was 80.6% (at 550 nm) and the sheet resistance was 8.3 Ω/sq. (e) The optical transmittance spectra with different Ag NWs weight densities

B. Plasma treatment

Fig. 3(e) shows the effect of plasma treatment time (with different radio-frequency power) vs. the value of R_s of Ag NWs TCEs of a sample with a weight density of around 87 mg/m^2. It was demonstrated that the increasing in the conductivity of transparent electrodes was significant when we increased the plasma treatment time. The sheet resistance of the TCEs drop by three to six orders of magnitude (120 W radio-frequency power: 7.38×10^7 Ω/sq and 5.76×10^4 Ω/sq before and after 30 min plasma treatment; 120 W radio-frequency power of plasma treatment decreased the sheet resistance from 6.7×10^7 Ω/sq to 18 Ω/sq after 30 min, as shown in Fig. 3(e). It appears that the improvement in the conductivity of the network became more significant when we increased the radio-frequency power.

The reason for this improvement can be considered as the removal of the residual insulating PVP layer coated on the Ag NWs and the cold-welding effect. In the first five minute, the value of R_s decreased dramatically owing to the rapid removal of insulating PVP on the Ag NWs,[19,20] and the following gentle decline of the curve indicates the residual PVP was completely cleaned with the NW junctions welded together (Fig. 3(f)). It can be observed that the junctions between Ag NWs were welded with proper plasma treatment time and radio-frequency power in Fig.3(c)-(e). Welding between the junctions was not achieved when the radio-frequency power is 120 W, according to Fig.3 (a)-(b) (the plasma treatment time is 30 min except for the control sample in Fig. 3(a)). In our study, we achieved the improvement of the conductivity of the Ag NWs networks and the damage to the flexible polymer substrates can be ignored as compared with high intensity pulsed light.[16] As an effective method for the post-treatment of Ag NWs network, plasma treatment can be employed for the preparation of Ag NWs based TCEs for large scale preparations.

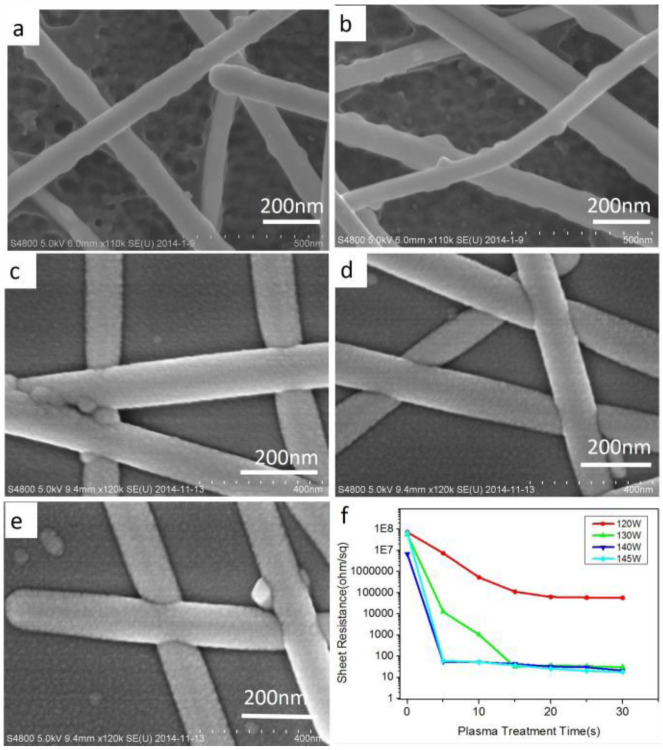

Fig. 3 (a) SEM image of the Ag NWs before the plasma treament; (b)-(e) SEM image of the AgNW after 30 min of plasma treament with different radio-frequency power: (b) 120W; (c) 130W; (d) 140W; (e) 145W; (f) effect of plasma treatment time versus surface resistance R_s

C. Selective deposition of Conductive Polymer Adhesive

We selectively deposited PEDOT:PSS on the Ag NWs film by adjusting the electrostatic spraying condition. Ag NWs were completely covered by PEDOT:PSS to form a uniform Ag NWs-PEDOT:PSS composite film (Fig.4(b)). As shown in Fig.4(c), it can be observed that PEDOT:PSS selectively distributed around Ag NWs networks, which can remain the percolated structure. Transparencies of different Ag NWs-PEDOT:PSS composite films were compared and the $T_{550\,nm}$ of Ag NWs covered with complete PEDOT:PSS coverage drop quickly (from 85.6 % to 78.9%) while $T_{550\,nm}$ of the other one was hardly observed (from 85.6 % to 85.3%). This

phenomenon suggests that the technology of selective deposition of the adhesive layer does not compromise the optical property. Both of them could improve the adhesion strength between Ag NWs network and the polymer substrates, but the selective deposition of the PEDOT:PSS adhesive layer is advantageous since the loss in optical property could be minimized.

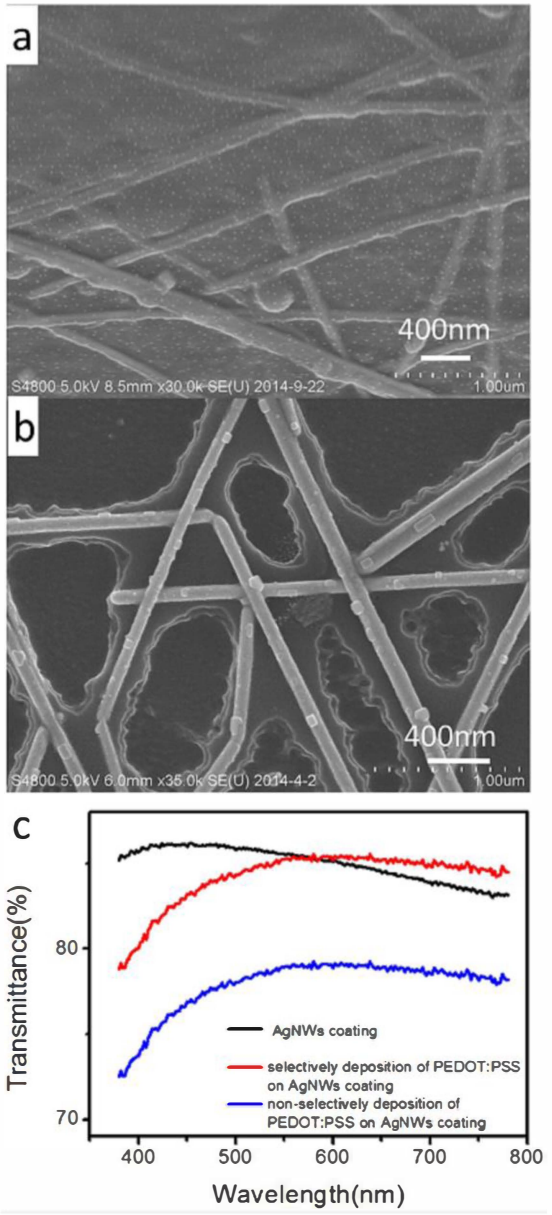

Fig. 4 (a) SEM image of the Ag NWs layer coverd with non-selectively deposition of PEDOT:PSS; (b) SEM image of the Ag NWs layer coverd with selectively deposited PEDOT:PSS layer; (c) optical transmittance spectra of original Ag NWs coating, Ag NWs coating with polymer adhesive and Ag NWs coating with selectively deposited polymer adhesive

IV. CONCLUSIONS

Here we demonstrated that the involvement of both electro-spraying and plasma treatment processes are essential for the fabrication of high quality Ag NWs based TCEs. In order to improve their performance characteristics, we optimized the spraying processing window, which rendered the best connectivity of junctions of Ag NWs with each other and with PEDOT:PSS, so as to enhance electrical conductivity of the film. Besides, the radio-frequency power of the plasma treatment is a crucial factor as well; we demonstrated that an optimal plasma treatment condition is critical to the cold-welding effect of the Ag NWs. Finally, the as-obtained TCEs show excellent electro-optical properties close to that of ITO.

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