Research Article

PEDOT:PSS Overcoating Layer for Mechanically and Chemically Stable Ag Nanowire Flexible Transparent Electrode

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We investigated the effect of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) deposition on the chemical and mechanical stability of Ag nanowire flexible electrodes. A large number of bending cycles, up to 500,000 cycles, were imposed on the Ag nanowire electrodes with and without PEDOT:PSS overcoating layer. In situ resistance measurement during bending tests revealed that the Ag nanowire electrode with PEDOT:PSS overcoating layer was mechanically reliable, showing a 21.9% increase in resistance after 500,000 cycles of bending. Scanning electron microscope images revealed that the failure of the Ag nanowire network occurred along with cracks initiated in the PEDOT:PSS layer, which resulted in the increase in resistance under bending. Furthermore, the PEDOT:PSS deposition enhanced the chemical stability of Ag nanowire electrode, which showed no significant increase in resistance after exposure in air for 50 days. Our study underscored that PEDOT:PSS is effective in protecting the Ag nanowires, while maintaining the high mechanical stability.

1. Introduction

Technological advances in flexible/wearable electronics require the development of robust electrodes that can tolerate severe mechanical bending [1–7]. The current choice for transparent electrodes is indium tin oxide (ITO) film, but the brittleness and the high processing temperature of ITO film make its use for flexible/stretchable electronics difficult [8, 9]. In addition, the shortage of indium reserves is continuously increasing material costs. Therefore, there have been several researches to develop novel materials to replace ITO. The potential alternatives to replace ITO are carbon nanotubes (CNT) [10, 11], graphene [12, 13], and metal nanowires [14–16]. Among the metal nanowires, Ag nanowire network is the most attractive candidate, owing to its high electrical conductivity and excellent optical transmittance [17–21]. Furthermore, Ag nanowire network is known to have outstanding mechanical flexibility, which is suitable for flexible/wearable electronics [2, 7, 22].

However, a limitation of Ag nanowires is their poor chemical stability on exposure to air [6, 19, 23]. The large surface-to-volume ratio allows the Ag nanowires to be easily oxidized when exposed to air, thereby degrading the electrical conductivity of the Ag nanowire network [2, 23]. Therefore, a suitable overcoating layer is required to prevent the Ag nanowires from surface oxidation; metal oxide [1, 3, 24], graphene [2, 6], and polymeric layer [25–27] are examples of the overcoating layers. PEDOT:PSS has been widely studied for the protective layer on Ag nanowires, due to its high conductivity and optically transparent property [25]. For example, Chen et al. reported that adopting the PEDOT:PSS reduced the sheet resistance of Ag nanowire network, without a significant loss of optical transparency [25]. In addition, the Ag nanowire with PEDOT:PSS overcoating layer was stable under ambient moisture, without significant loss of electrical conductivity [25].

However, since the main goal of the Ag nanowire network is its use for flexible electronics, understanding of the mechanical reliability of the Ag nanowire networks with PEDOT:PSS layer is crucial. To satisfy the requirements for reliability in the actual operational conditions of electronic devices, the conductor should be able to withstand a bending
strain of more than 300,000 cycles [7]. But no systematic studies have previously been conducted on the mechanical reliability of Ag nanowire network with PEDOT:PSS layer under large cycles of bending.

This work systematically investigated the effects of PEDOT:PSS layer on the mechanical and chemical stability of Ag nanowire network. Ag nanowires on a flexible polyethylene terephthalate (PET) substrate were coated with PEDOT:PSS by using a spin coater. By imposing a large number of bending cycles, 500,000 cycles, while measuring the resistance in situ, the mechanical reliability of the Ag nanowire with PEDOT:PSS layer was systematically evaluated. The deformation behavior of Ag nanowire with PEDOT:PSS layer was further confirmed by analyzing the microstructure before and after bending using scanning electron microscopy (SEM). In addition, the Ag nanowires with and without PEDOT:PSS layer were exposed to air for 50 days, to confirm the enhanced chemical stability from the PEDOT:PSS layer.

2. Experiments

2.1. Fabrication and Characterization of Ag Nanowire Electrode with PEDOT:PSS Layer. The Ag nanowires were synthesized by using a well-known polyol process. The details of the synthesizing method can be seen in [16]. The Ag nanowire solution was deposited on a flexible PET substrate by doctor blading. The height of the blade was fixed as 150 μm, and the blading speed was 10 mm/sec. The as-coated Ag nanowire electrodes were then annealed at 120 °C for 10 min in air. The sheet resistance of the Ag nanowire electrodes was 15.1 ± 1.3 Ω/□, and the optical transmittance was 86.1 ± 0.7%. PEDOT:PSS aqueous solution with the solid content of ~1.3 wt% (PH1000, Clevios™) was used in the study. The PEDOT:PSS was coated on the Ag nanowire electrodes by a spin coater. The spin-coating time and rpm were fixed at 30 seconds and 5,000 rpm, respectively. The PEDOT:PSS coated Ag nanowire electrodes were baked at 120 °C for 5 min in air. The thickness of the PEDOT:PSS layer on Ag nanowire electrodes was measured as 200 nm. PEDOT:PSS deposition decreased the sheet resistance of Ag nanowire electrode to 11.6±0.4 Ω/□ and the optical transmittance to 83.8±1.1%. The continuous PEDOT:PSS film was confirmed to increase the sheet resistance of the Ag nanowire electrodes while decreasing the optical transmittance. The optical transmittance was measured by UV-Vis spectrometry (Haze-Gard I) from BYK-Gardner Additives & Instruments. Four-point probe (FPF-2400, Dasol Engineering Co., Ltd.) was used to measure the sheet resistance of the Ag nanowire electrodes. The surface morphology analysis was performed by field-emission SEM (FE-SEM, Phillips, XL30 ESEM-FEG).

2.2. Bending Fatigue Test. Cyclic bending fatigue tester (CK Trading Co. Ltd.) was used to perform the cyclic bending tests on the Ag nanowire electrode with and without PEDOT:PSS layer (Figure 1). A detailed explanation of the bending fatigue tester can be found in [7]. In brief, the Ag nanowire electrodes were mounted on two plates using screw bolts, and Cu pads at the end of each plate where the Ag nanowires were in contact enabled in situ resistance monitoring. The horizontal movement of the lower plate imposed repeated bending strain on the specimens. The bending strain could be calculated using the equation \( \varepsilon = \frac{y}{R} \), where \( y \) is the distance from the neutral plane and \( R \), the radius, is the half value of the distance between the plates. Here, the gap between the two plates was fixed as 6 mm, which corresponds to a bending strain of 2.1%. The bending speed was 300 cycles/min, and the total number of bending cycles was 500,000 cycles.

3. Results and Discussion

3.1. Mechanical Reliability of Ag Nanowire Electrode with PEDOT:PSS Layer. To investigate the effect of the PEDOT:PSS layer on the mechanical reliability of Ag nanowire electrode, a large number of bending cycles, 500,000 cycles, were imposed on the Ag nanowire electrode with and without PEDOT:PSS layer. The Ag nanowire electrodes were prepared to have an initial sheet resistance of ~15.1 Ω/□, which was then decreased to ~11.6 Ω/□ after coating the PEDOT:PSS layer. Figure 2(a) shows the cyclic bending test results of bare Ag nanowire electrode and PEDOT:PSS coated Ag nanowire electrode. The result of Ag thin film with 100 nm thickness tested under the same testing condition was presented together for comparison. The mechanical reliability of the Ag nanowire electrode and the PEDOT:PSS coated Ag nanowire electrode was excellent compared to that of Ag thin film. The increase in fractional resistance of Ag thin film was 385.2% after 500,000 cycles of bending, while the Ag nanowire electrode and the PEDOT:PSS coated Ag nanowire electrodes showed 20.8% and 21.9% increase, respectively. The corresponding sheet resistance change of the Ag nanowire electrodes with and without PEDOT:PSS overcoating layer as a function of bending cycles can be seen in Table 1.

| Cyclenumber | 0  | 1000 | 10,000 | 100,000 | 500,000 |
|------------|----|------|--------|---------|---------|
| Without PEDOT (ohm) | 15.0 | 15.4 | 16.0 | 17.1 | 18.3 |
| With PEDOT (ohm) | 11.7 | 12.7 | 13.2 | 13.8 | 14.2 |

The excellent mechanical reliability of the Ag nanowire networks is known to be due to their nanoscale dimension.
and the geometrical advantage of the network [2, 7, 22]. In case of the Ag thin film, the dislocation accumulation at the film/substrate interfaces during cyclic bending causes extrusion formation, where the cracks are initiated and propagated as the bending cycles increase further [7]. The cracks can act as the obstacle for the electrical current flow, which increases resistance. On the other hand, the size-dependent plasticity and the low density of surface defects observed in metal nanowires result in high strength that approached the theoretical strength, which is defined as $E/10$ [2]. Therefore, the individual nanowire with high strength can bear more bending strain than can the bulk material. In addition to the high strength, the network geometry is a reason for the excellent mechanical stability of Ag nanowire electrodes. Under bending or stretching condition, the nanowire network can release the imposed bending strain, by adjusting its network along the direction of deformation [2, 7, 22]. Furthermore, the dislocation accumulation observed in the thin films is difficult to occur in the network geometry [2, 7, 22], which can be another reason for the enhancement of mechanical reliability. Although the PEDOT:PSS layer has a continuous blanket structure, the high flexibility of PEDOT:PSS film [28, 29] made the Ag nanowire network sustain its excellent mechanical reliability; thus, the gap of increase in fractional resistance between the nanowire networks with and without PEDOT:PSS layer was small after 500,000 cycles (Figure 2(b)).

To further confirm the effect of PEDOT:PSS layer on the deformation behavior of Ag nanowire electrode, the surface morphology was analyzed for the bare Ag nanowire electrode and the PEDOT:PSS coated Ag nanowire electrode using SEM. Figure 3 presents the SEM imagery of each specimen before and after cyclic bending tests. The bare Ag nanowire electrode showed network structure (Figure 3(a)); Figure 3(d) shows that, after coating with PEDOT:PSS, the network structure was buried in the PEDOT:PSS film. After 1,000 cycles of bending, a number of failures of the individual Ag nanowires were observed (Figure 3(b)), while the cracks were initiated in the PEDOT:PSS layer, along which the Ag nanowires were also broken together (Figure 3(e)). Once the damage (such as breakage of Ag nanowire or cracks in PEDOT:PSS layer) initiated in the electrodes, the applied stress could be concentrated near the damaged area, which resulted in the propagation of the damage, consequently causing the detaching of a part of the conductive layer (Figures 3(c) and 3(e)). Since there was no current path in the damaged area where the conductive layer was removed, the resistance would increase rapidly as the fraction of damaged area increased.

3.2. Ambient Stability of Ag Nanowire Electrode with PEDOT:PSS Layer. The enhancement of chemical stability of Ag nanowire electrode by adopting a PEDOT:PSS layer was investigated by exposing the electrodes to ambient air for 50 days. The results of sheet resistance change depending on the exposure time are shown in Figure 4. While the sheet resistance of bare Ag nanowire electrode was remarkably increased from $\sim 15.2$ to $\sim 598.8 \, \Omega / \square$ after exposure in air for 50 days, there was no significant increase in sheet resistance of the Ag nanowire electrode with PEDOT:PSS layer. The SEM imagery taken for each specimen after exposure for 50 days shows that the oxide particle covered the surface of the bare Ag nanowires electrodes (Figure 5(a)), but the Ag nanowire electrode with PEDOT:PSS layer showed no observable oxidation (Figure 5(b)). The PEDOT:PSS layer was effective in preventing the Ag nanowire electrodes from contact with the oxygen or water in air, thereby suppressing surface oxidation. Surface oxidation was known to deteriorate the electrical conductivity of Ag nanowires, due to the composition change from Ag to $\text{Ag}_2\text{O}_3$ or $\text{Ag}_2\text{S}$ as well as due to the reduced cross-sectional area by oxidation [2]. Therefore, the suppressed surface oxidation observed in the Ag nanowire electrode with
Figure 3: SEM images of (a–c) Ag nanowire electrodes with PEDOT:PSS overcoating layer and (d–f) bare Ag nanowire electrodes as a function of bending cycles: (a, d) before bending, (b, e) after 1,000 cycles, and (c, f) after 500,000 cycles.

Figure 4: Sheet resistance change of Ag nanowire electrodes with and without PEDOT:PSS layer as a function of exposure time to air at room temperature. PEDOT:PSS is in agreement with the lack of change in sheet resistance after exposure in air for 50 days.

4. Conclusion

In summary, the bending fatigue behavior of PEDOT:PSS coated Ag nanowire electrodes was explored by using the cyclic bending tester, which is capable of imposing a large number of cycles of bending up to 500,000 cycles when monitoring the resistance in situ. The cyclic bending fatigue tests revealed that the Ag nanowire electrode with PEDOT:PSS layer was highly flexible and could sufficiently withstand the high number of cycles of bending. The increase in fractional resistance of the PEDOT:PSS coated Ag nanowire
electrodes was ~19 times smaller than that of Ag thin film. Furthermore, the ambient stability of Ag nanowire electrodes was remarkably enhanced by adopting the PEDOT:PSS layer, showing no increase in sheet resistance after exposure in air for 50 days. The PEDOT:PSS was effective in protecting the Ag nanowires from surface oxidation, by preventing the Ag nanowire from contact with the oxygen or water in air. Our study highlighted that PEDOT:PSS is a suitable candidate. The results of the deformation behavior of the Ag nanowire electrodes with PEDOT:PSS layer will provide practical guidance for applications of a hybrid system for flexible/wearable electronics.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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