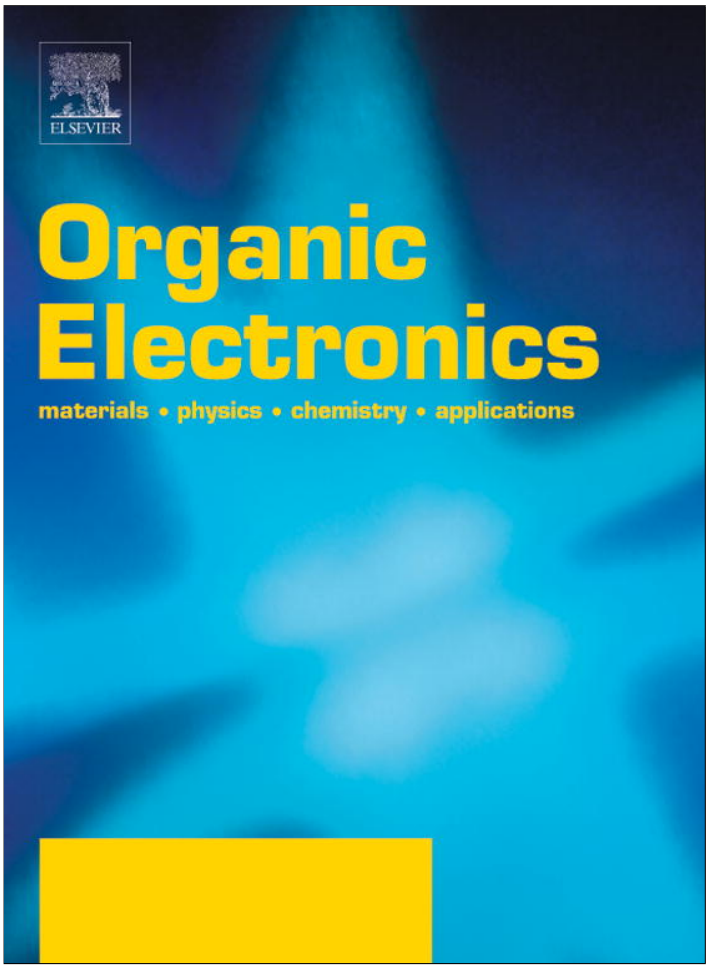


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# Electrical performance of the embedded-type surface electrodes containing carbon and silver nanowires as fillers and one-step organosoluble polyimide as a matrix

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ABSTRACT

Embedded-type surface electrodes with silver nanowire (AgNW) and carbon nanotube (CNT) as conductive fillers and organosoluble polyimide (PI) as a matrix were investigated for their electrical conductivity and electrical durability under cyclic bending. The chosen polyimide was constituted with 4,4′-oxydiphthalic dianhydride and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane through a one-step process. Two types of surface electrodes of CNT/PI and AgNW/PI were prepared at 90 °C. The flexible CNT/PI and AgNW/PI surface electrodes not only had high electrical conductivities of 6.3 and 100 S/cm, respectively, after 30 spraying cycles but also kept electrical durability after 1200-time bending tests. The ITO-coated ITO/PI and ITO/AgNW/PI electrodes, for a comparative purpose, had severe electrical failure under cyclic bending.



## 1. Introduction

Flexible electronics, which have received much attention because of their lightweight and feasibilities in bending, folding, and mounting to surface, can be potentially applied for many electronic devices such as large-area display, light-emitting diode, solar cell, semiconductor, sensor etc. [1,2]. CNT is one of the major conductive materials for electrode in flexible electronics. It has been built as a conductive network on substrates to form a surface-covered electrode or blended with polymers to form a composite-type electrode, by using vacuum infiltration, dip coating, dry transfer, post-treatment, ink-jet printing, spray coating, or in situ polymerization [3,4]. The CNT-based contact and interconnect used for flexible electronics have been an active research field [5–9]. AgNW with higher electrical conductivity ($\sigma$) is also a potential electrode material. In general, AgNWs for electrical contact and interconnect have been directly covered on substrates as a conductive network, followed by a heating treatment to hold AgNWs with the partial polymer melting on the surface of polymer substrate for improving adhesion and connection [10–14]. There are few reports on the AgNW-based electrodes prepared in the form of an AgNW/polymer composite layer on the top surface of a flexible substrate [15,16].

Polyimide (PI), which features outstanding thermal stability with a high glass transition temperature of 360 °C, chemical inertness, low CTE (3.4 ppm/K), and excellent tensile strength, has been already used as high-performance interconnect component and substrate in microelectronic industries [17–20]. There are two major methods for preparing PI, i.e. one-step and two-step processes. Most of the processes adopt a two-step method by reacting diamine with dianhydride monomers followed by an imidization process at 300 °C. However, this method has some drawbacks, i.e. the nonstability of the formed poly(amic acid) (PAA) precursor and the difficulties in liberating water during imidization and in controlling the imidization process [21]. For a one-step method, PI is

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synthesized by mixing monomers at room temperature in a high-boiling-point solvent, followed by heating at 190–210 °C for imidization. The advantages for this method include lower imidization temperature, high molecular weight of PI, and the easy removal of the water byproduct during an imidization process [22].

Electrical conduction of polymer can be improved by laying conductive CNTs into a percolation network. Only the surface-covered CNT electrodes with aligned fillers or a high CNT content can display high electrical conductivity of 17–200 S/cm [23–25]. These types of electrodes have been routinely prepared by non-conventional processing approaches, e.g. vacuum filtration and coagulation spinning. Comparing with non-conventional approaches, CNT/polymer composite electrodes made by conventional approaches, such as solution casting and melt mixing, are difficult to achieve high electrical conductivity. There are only some reports with $\sigma > 1$ S/cm [26,27]. Ramasubramaniam et al. reported a CNT/polycarbonate composite with $\sigma$ of 4.81 S/cm [26]. Grossiord et al. reported a CNT/polystyrene composite made by resin transfer molding having a $\sigma$ value of 10 S/cm [27]. By using PI as a matrix, the improvements in its electrical conductivity remain urgent [28–30]. Recently, Yuan et al. designed and synthesized a two-step PAA as a matrix and simultaneously as a dispersant to improve its compatibility with CNTs during a solution-cast process. After imidization at 350 °C, CNT/PI hybrid composite films had high electrical conductivity of 38.8 S/cm at a 30 wt.% CNT content [31]. For those above-mentioned studies, their CNT/PI composites were prepared with two-step PIs and did not reach the expected $\sigma$ values.

In addition to CNT-based electrodes, some researchers have begun to fabricate AgNW-based electrodes [32–37]. However, the reports based upon surface-covered or composite-type AgNWs/PI electrodes were limited [38]. In this study, the PI-based and embedded-type surface electrodes with CNT and AgNW as conductive fillers were prepared by spraying a CNT or AgNW stock solution into conductive networks, followed by drop coating a PI layer and drying at 90 °C for 24 h to form the embedded-type surface electrodes, where a conductive composite layer was formed on the top surface of a flexible PI substrate. Our organosoluble PI was synthesized by a one-step process with the monomers of 2,2-bis(3-amino-4-hydrooxyphenyl)hexafluoropropane (6F-OH diamine) and 4,4′-oxydiphthalic dianhydride (ODPA) [39]. The low-temperature process of our surface electrodes at 90 °C can avoid high-temperature damages to other organic components. The effects of spraying cycle of the nanowire stock solutions and an outer sputtered ITO coating upon electrical conductivity of our embedded-type surface electrodes are investigated. Electrical durability of the surface electrodes under stressing was evaluated by a cyclic bending test at a fixed bending angle of 60°.

## 2. Experimental

Multi-wall CNTs were purchased from Nanocyl Co. Ltd., Korea. Ag nanowires were synthesized *via* a polyol process by reducing silver nitrate with ethylene glycol at ~160 °C for 2 h under the existences of Pt seeds for nucleation and poly(vinyl pyrrolidone) (PVP) as a template. CNT and AgNW stock solutions of 0.0974 vol.% were prepared by dispersing their own nanowires in ethanol with the aid of ultrasonication for 1 h. Our transparent and organosoluble polyimide was synthesized by a one-step polycondensation reaction between 6F-OH diamine and ODPA in m-cresol with isoquinoline as a catalyst. The imidization reaction was executed at 200 °C for 15 h, after that PI was precipitated from methanol and dried at 90 °C for 24 h. The PI stock solution of 5 vol.% was formed by dissolved precipitated PI fibers in *N*,*N*-dimethylacetamide (DMAc). Embedded-type surface electrodes in this study were divided into four kinds of systems. The first two systems were the CNT/PI and AgNW/PI. Fig. 1 shows the illustrative protocol procedures for preparing these two systems. The CNT/PI and AgNW/PI systems were individually prepared by spraying their own stock solutions for 6, 8, 12, 20, and 30 times on 1 × 1 cm microscope slides heated at 110 °C. A PI stock solution of 0.2 ml was drop coated onto the nanowire-covered slides, followed by drying at 90 °C to complete the fabrication procedures of surface electrodes. The third system of ITO/AgNW/PI was prepared by radio-frequency (rf) sputter coating of ITO films at 50 W and 200 °C for 20 min onto the 20 times-coated AgNW/PI (AgNW20/PI)) embedded-type electrodes, abbreviated as the ITO20/AgNW20/PI electrode. The last system is ITO20/PI, which was made by depositing ITO film on polyimide substrates with the same sputtering condition as for the third system and was also used as a reference for comparison purpose.

Field-emission transmission electron microscopy (FE-TEM, Philips Tecnai F20 G2) was used to reveal the detailed nanostructures of as-received CNTs and self-synthesized AgNWs. Surface morphology of our embedded-type electrode systems was investigated with a Dual-Beam Field Emission Focused Ion Beam (FIB, FEI Quanta 3D FEG) instrument. For the durability experiment, the PI substrates with surface electrodes were clamped by two alligator clips at two edges, followed by different cyclic bending numbers at a constant angle of 60°, as shown in

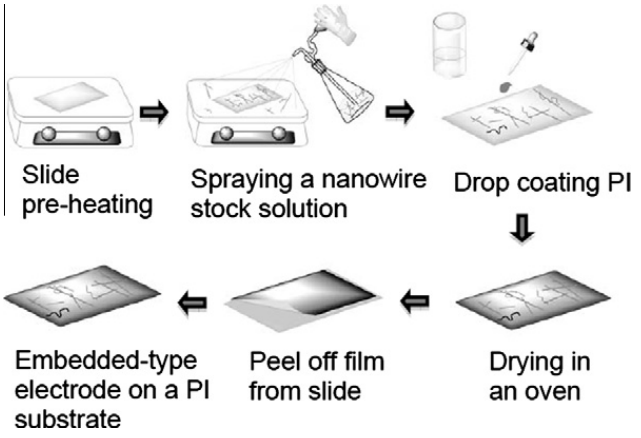


**Fig. 1.** Illustrative protocol procedures for preparing embedded-type surface electrodes with CNT and AgNW as conductive fillers and polyimide as a matrix.

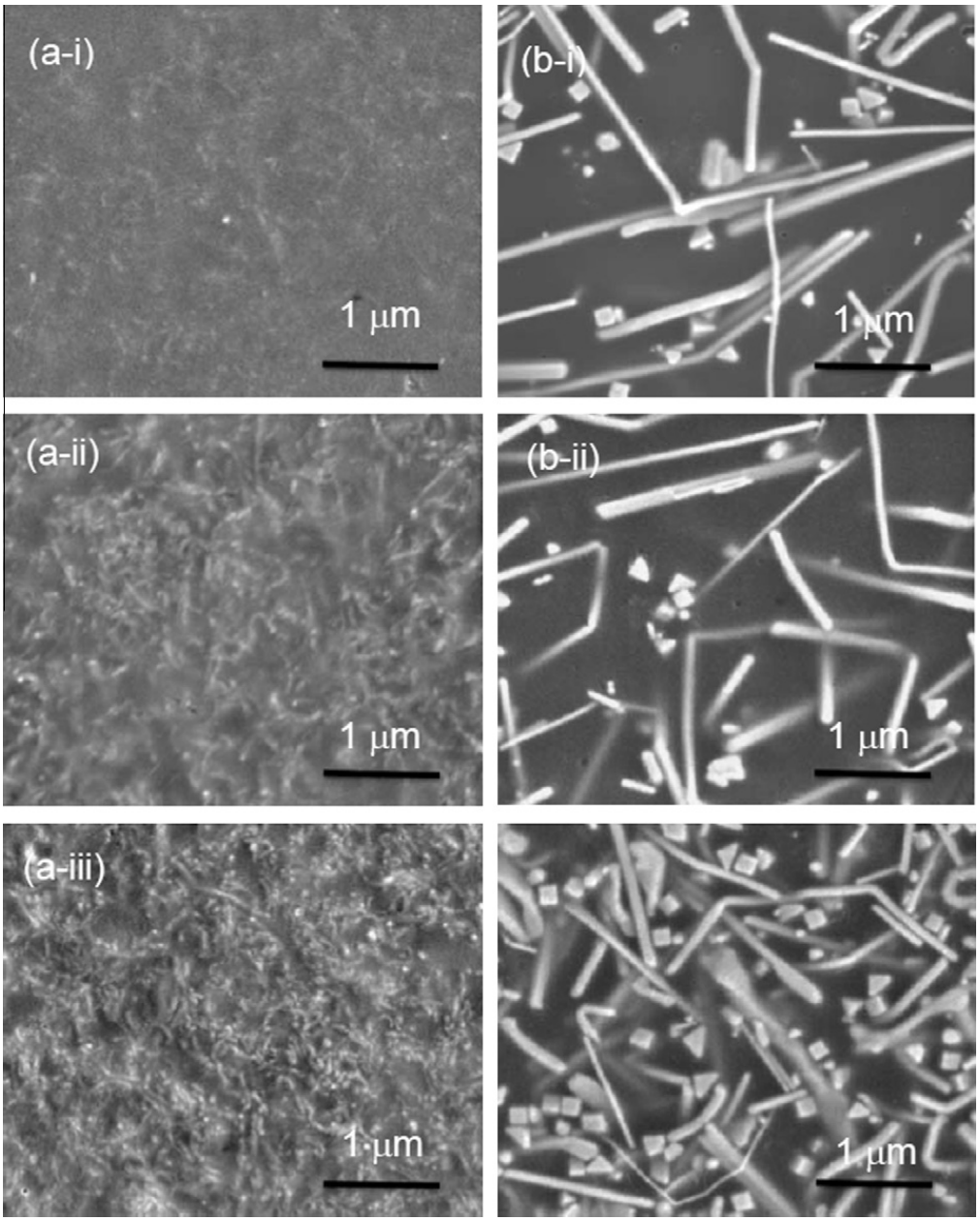


**Fig. 2.** FIB images of the embedded-type (a) CNT/PI and (b) AgNW/PI surface electrodes with the spray cycle of (i) 6, (ii) 12, and (iii) 30 times.

the insert in Fig. 4. A Field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) was used to observe the specimens after bending tests. Electrical conductivity of the embedded-type electrode before and after cyclic bending was measured by a four-point probe method (Signatone four-point probe station; Keithley 220 current source; Keithley 182 digital voltmeter). The bent specimens were also examined by FE-SEM.

## 3. Results and discussion

Fig. 2 shows FIB images of the embedded-type (a) CNT/PI and (b) AgNW/PI surface electrodes with the spray cycles of (i) 6, (ii) 12, and (iii) 30 times. CNT/PI electrodes were composed of a PI matrix and the as-received CNTs of 20–40 nm in diameter and 5–15 μm in length. The solu-

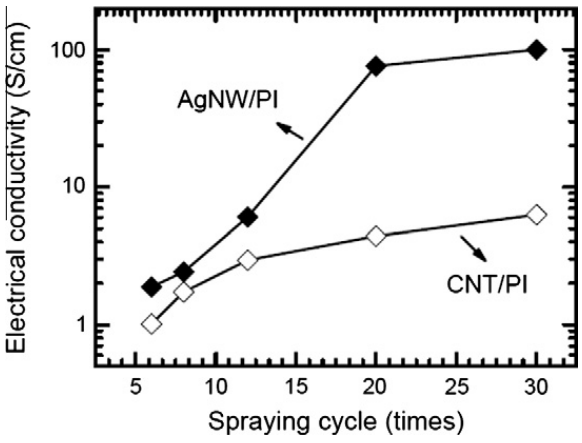


**Fig. 3.** Electrical conductivity analyses of the embedded-type CNT/PI and AgNW/PI surface electrodes at different spray cycles.

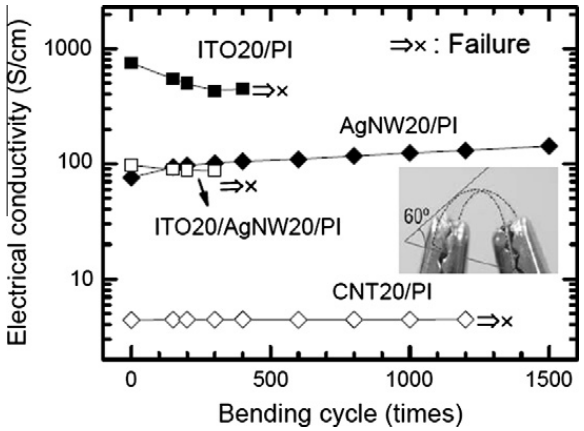


**Fig. 4.** Variation in electrical conductivity of different surface electrodes with the bending cycle. The insert is the photograph to show the bending configuration.

tion-cast PI substrate had a layer thickness of 7.5 ± 0.3 μm. CNT/PI surface electrodes had layer thicknesses increased from 0.68 ± 0.09 μm to 1.47 ± 0.07 μm as the spray cycles increased from 6 times to 30 times. After spraying for 12 times, the electrode surface became rougher due to the aggregation of CNT bundles. To our knowledge, although chemical or surfactant treatments on CNTs can uniformly disperse CNT bundles, these modifications may interrupt the conductive paths of CNTs. Compared with CNT/PI electrodes, AgNW/PI electrodes with layer thicknesses of 0.85 ± 0.07–2.87 ± 0.48 μm displayed loose packaging of AgNWs, even spraying cycles up to 30 times. The conduction networks of AgNW/PI electrodes consisted of AgNWs with a diameter of 106 ± 47 nm and a length of 3.07 ± 1.58 μm, while some Ag particles of 0.2 μm intermixed with AgNWs.

Fig. 3 displays electrical conductivity analyses of the embedded-type CNT/PI and AgNW/PI surface electrodes after different spray cycles. After 6 spray cycles, CNT/PI and AgNW/PI surface electrodes reached percolation threshold to show the electrical conductivity. For both electrodes, the electrical conductivity increased with the increase in the spray cycle. CNT/PI and AgNW/PI surface electrodes with the spray cycle less than 10 times had lower electrical conductivity. AgNW/PI surface electrodes with the spray cycle more than 20 times had much higher electrical conductivity than the CNT/PI ones. The reason was attributed to the higher electron-transport ability for Ag and the denser conductive network formed at more spray cycles. After 30 spray cycles, our CNT/PI and AgNW/PI surface electrodes reached their highest electrical conductivities of 6.3 and 100 S/cm, respectively. These values were comparable to other PI-based composite electrodes [26–29]. In order to improve the electrical conductivity of CNT/PI electrodes at fewer spray cycles, AgNWs had been incorporated into CNT/PI surface electrodes.

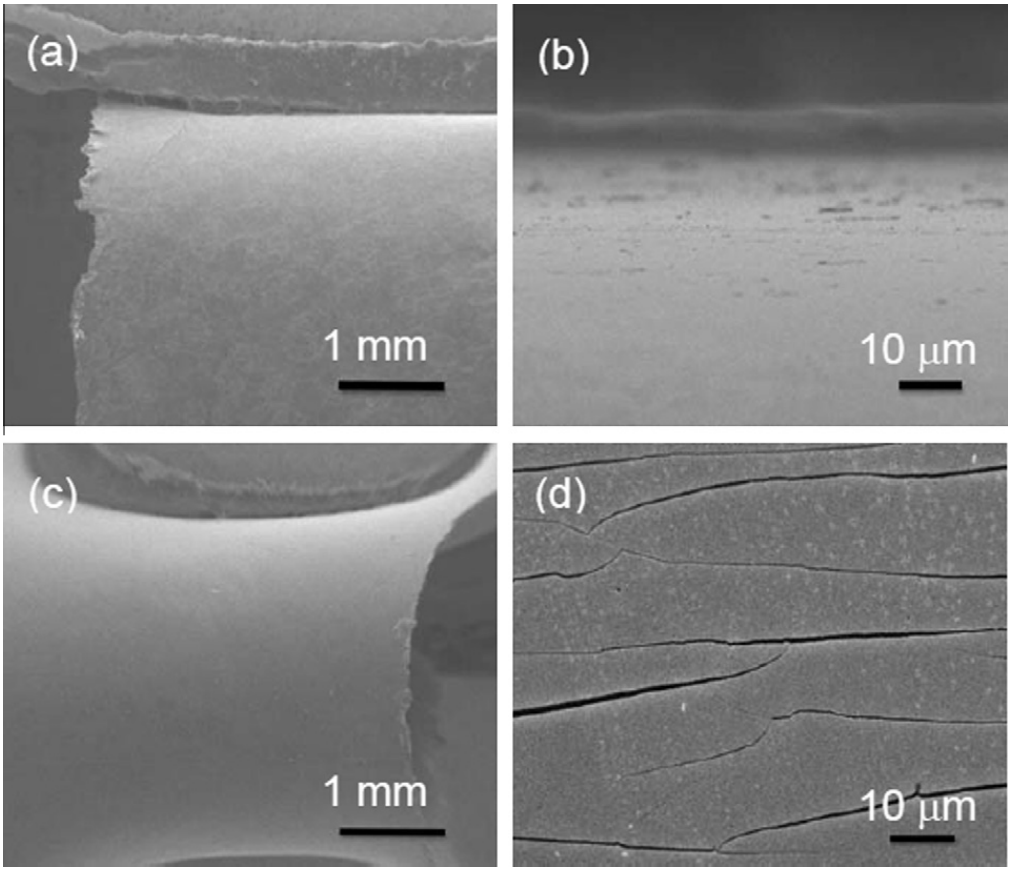


**Fig. 5.** FE-SEM images of (a, b) AgNW20/PI and (c, d) ITO20/PI surface electrodes that underwent 200 bending cycles. The images in (b, d) were taken at a higher magnification.

Fig. 4 demonstrates the variation in electrical conductivity of different surface electrodes with the bending cycle. The insert is to show our bending configuration. The surface electrodes involved embedded-type CNT and AgNW electrodes and the ITO-coated AgNW/PI and ITO/PI electrodes. Our CNT20/PI and AgNW20/PI electrodes obtained by spraying their individual solution for 20 times had the $\sigma$ values of 4.4 and 75.8 S/cm, respectively, before bending tests. Electrical performance of this CNT/PI electrode remained intact up to 1200 bending cycles then became unstable after 1500 cycles. However, the AgNW20/PI electrode remained active and slightly increased $\sigma$ to 142.7 S/cm after 1500 bending cycles due to the AgNW alignment to force the formation of better contacts. For the ITO-coated AgNW20/PI electrodes, the coverage of the sputtered ITO film on the AgNW/PI electrode had no benefits in increasing the electrical conductivity of AgNW/PI electrode due to the failure in forming a continuous ITO film. At the meantime, the long-lasting performance of AgNW/PI electrode in electrical conductivity deteriorated with a bending life only up to 300 times, as the ITO coating was deposited. For the comparative purpose, the ITO/PI electrodes with ITO films deposited for 20 times, symbolized as ITO20/PI, showed the highest conductivities of 800 S/cm, but they failed under the bending tests no more than 400 cycles. It is well known that ITO-covered surface electrodes had high electrical conductivity. However, this electrode on a flexible polymer substrate suffers a problem of a mismatch in elastic modulus, which can lead to the ITO cracking under cyclic bending and the electrical failure.

Fig. 5 shows the FE-SEM images of (a, b) AgNW20/PI and (c, d) ITO20/PI surface electrodes that underwent 200 bending cycles. The images in Fig. 5(b) and (d) were taken at a higher magnification. After 200 bending cycles, the ITO/PI electrode showed the parallel cracks, perpendicular to the loop tensile loading. This cracking led to its decrease in electrical conductivity (Fig. 4). However, the AgNW20/PI electrode remained intact with no observable cracks (Fig. 5(a) and (b)) and no degraded conductivity (Fig. 4).

## 4. Conclusions

Embedded-type surface electrodes with CNT and AgNW as conductive fillers and polyimide as a matrix have been successfully fabricated by constructing a conductive network in a composite layer on the surface of flexible PI substrates. Because our surface electrode films adopted the one-step organosoluble PI as a matrix, therefore it can be fabricated at 90 °C instead of 300 °C by using the poly(amic acid) route. This low temperature process for our surface electrode can avoid the high-temperature process to damage other organic components. Our CNT/PI and AgNW/PI surface electrodes have electrical conductivity of 6.3 and 100 S/cm, respectively, after the spraying cycle of 30 times. CNT20/PI and AgNW20/PI electrodes can survive at 1200 and 1500 bending cycles, respectively, without degrading their electrical performance, while the ITO-coated electrodes had a shorter life under cyclic bending.

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