Inkjet-print patterned transparent conductive CNT films

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Abstract

Using a chemical radical we modified the surface property of PET substrates. The chemically treated substrate surface improved dispersion of CNTs on substrate and provides suitable adhesion of CNTs to substrate. In addition, an ink-jet printed patterning technique effectively improved the transparency of transparent conductive CNT composite films.

1. Introduction

CNTs are promising candidates for transparent conductive electrode materials in flexible displays. For applications, we have to overcome several obstacles such as bundle formation or aggregations of CNTs due to the mutual interaction between CNTs and a poor adhesion of CNTs to substrate materials. Using chemical radicals we changed the properties of substrate surface. The modified surface property improves the dispersion of CNTs on substrate and provides suitable adhesion of CNTs to substrate.

2. Results

The acid treated thin multi-walled CNTs [1] were well dispersed without any surfactants in the isopropyl-alcohol (IPA) by ultrasonication for 10 min. The carboxyl functional radical through the nitric and sulphuric acid treatment is easy to dispersion of CNTs in hydrophilic solution. In addition to form a uniform film on substrate and to get stable electric property without CNTs coming out of transparent conductive CNTs film, plastic substrates is required to modify the surface property.

The surface of PET (poly ethylene terephthalate) substrate was changed to more hydrophilic through the 3-aminopropyltriethoxysilane (3-ATS) treatment. The PET film with an inkjet printed pattern was immersed in the mixture solution of hexane and 3-ATS (5:1 Vol.) for 40sec. Figure1 shows the wet-ability of deionized water to PET and 3-ATS treated PET substrates with inkjet printed patterns. In figure 1(B), the surface property was modified to more hydrophilic than that without 3-ATS treatment (figure 1(A) and wet-ability was improved.

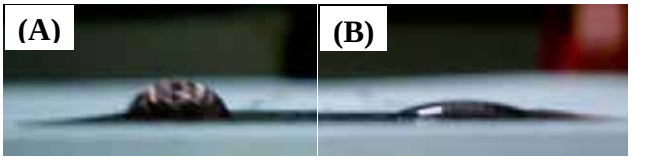

Figure 1. The photograph for the wet-ability of D.I. water to PET substrates: (A) without 3-ATS treatment and (B) with 3-ATS treatment.

The CNTs film was formed on 3-ATS treated PET substrate. The PET film with anti-cross striped inkjet printed pattern went through the 3-ATS treatment process. And then CNTs dispersed in IPA were sprayed on the PET substrate. The acid treated thin multi-wall CNTs were dispersed about 5 wt. (%) in IPA and the solution of about 6 ml was sprayed.

In figure 2(A) shows the FE-SEM (JEOL, JSM-6700) image of dispersed CNTs on PET substrate with 3-ATS treatment. The formed transparent conductive CNTs film shows a partial CNTs lump and vacancies of PET surface. Figure 2(B) and (C) are the photograph images of CNTs film formed on PET substrate. By removing the inkjet printed pattern, the transparent conductive CNTs film shows the improvement of about 63.2 % in the transparency property. The inkjet printed pattern was removed through ultrasonication in toluene for several seconds. As a result, chequered CNTs electrode was survived on the PET substrate (see a figure 2(C)). The transmittance was measured at 600 nm using UV-

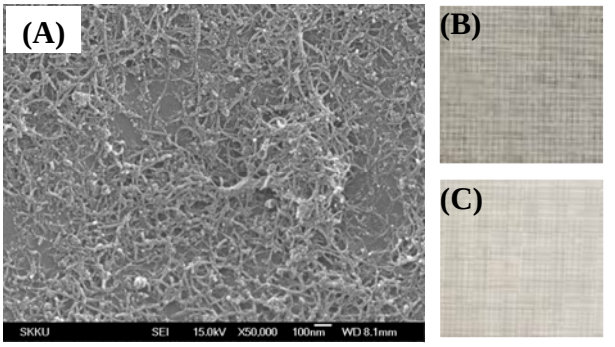

Figure 2. The CNTs film formed on 3-ATS treated PET substrate: (A) FE-SEM image of dispersed CNTs, and photograph images of CNTs film on PET substrate: (B) before and (C) after removing the inkjet printed pattern.

visible spectrometry (SCINCO, UV S-2100). The transmittance of CNTs film for before and after removing the inkjet pattern in figure2 was about 40.2 %(B) and 65.6 %(C).

The stable and reliable properties of transparent conductive film using CNTs are able to guarantee by improving the adhesion of CNTs to substrate. Many other groups reported the solutions about that using CNT surfactant. [2-3] Our group was proposed to use polyvinyl alcohol (PVA) as an adhesion layer in previous results. In this study, we tried a direct reaction method between CNTs and PET substrate. The 3-ATS treatment was suitable for not only the strong adhesion but also the good dispersion of acid treated CNTs to PET substrate. The adhesion ability of dispersed CNTs was checked up by tape test. In figure3, the come-out of CNTs from the chequered transparent conductive CNTs film was decreased in (B)-sample with 3-ATS treatment than (A)-sample without 3-ATS treatment. The same amount of CNTs-IPA solution was sprayed on each substrate.

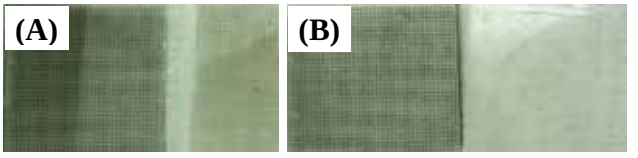

Figure 3. The tape test for CNTs adhesion ability to plastic substrates: (A) without 3-ATS treatment and (B) with 3-ATS treatment.

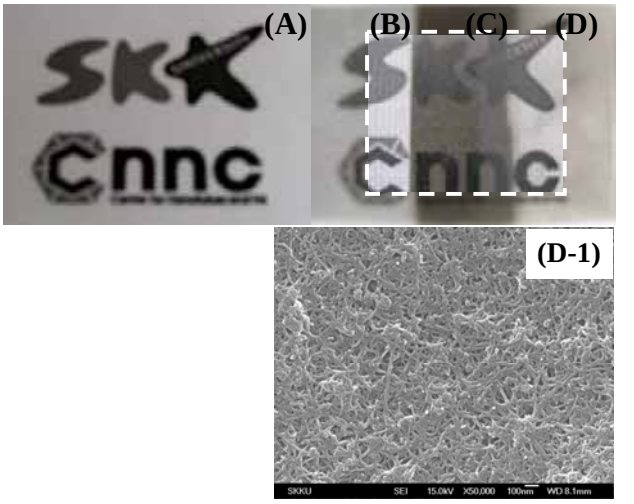

Figure 4. The photographs of transparent film using CNTs: (A) without CNTs transparent film, (B) inkjet printed PET film, (C) CNTs film on PET substrate with inkjet printed pattern, and (D) chequered CNTs transparent film on PET substrate. The high focused image inserted. (D-1) FE-SEM image of dispersed CNTs at (D) film.

For completely covered CNTs transparent conductive film, the more CNTs-IPA solution was sprayed on PET substrate with the inkjet printed pattern. The more CNTs make for the better electric conductivity. The CNTs-IPA solution of about 45 ml was sprayed. Figure4 shows the FE-SEM image (D-1) of dispersed CNTs on PET substrate with 3-ATS treatment. The CNTs looks like a randomly laminated film on PET substrate. The photographs of transparent film using 45 ml CNTs-IPA solution are shown in figure 4. We can compare the transparency of the transparent conductive CNTs film under a common fluorescent light source as mentioned experiment procedures (B, C, and D). The CNTs transparent film was piled up on paper with logos (figure 4A) printed the different freshness of inks. In figure4, (B) shows the inkjet printed anti-check pattern on PET film, (C) shows CNTs film formed on PET substrate with inkjet printed pattern, and (D) shows the chequered CNTs transparent film after removing the inkjet printed pattern. The transmittance of CNTs film for before and after removing the inkjet pattern in figure4 was about 30 %(C) and 45 %(D). By removing the inkjet printed pattern, the transparency property of CNTs film was improved about 50 %.

The thickness of sprayed CNTs on PET substrate was measured using atomic force microscope (AFM: THERO-Microscopes, USA). The CNTs on PET substrate piled up about 0.1 um and about 1.3 um when the 5 wt. (%) CNTs-IPA solution was sprayed about 6 ml and 45 ml, respectively.

The room temperature two-probe DC conductivity of films is shown in figure5. The plot of sample(A: see a figure 2(A)) is for the CNTs film formed by spraying of 6 ml CNTs-IPA solution. The plot of sample(B: see a figure 4(D-1)) is for the CNTs film formed by spraying of 45 ml CNTs-IPA solution. For 6 ml CNTs-IPA solution spray, the two-probe conductivity of CNTs film on 3-ATS treated PET substrate was approximately the same order of magnitude as films on PET substrate. As shown in IV curve of figure5, the resistance of CNTs films (6 ml: sample A and 45 ml: sample B) on 3-ATS treated PET substrate was 3.09E+04 ohm and 1.74E+05 ohm, respectively. The length between two-probe and width of sample was the same size. The resistance and sheet resistance by theoretical calculation was approximately the same. The amount of CNTs was increased but the electric conductivity was not improved as the resistance was increased approximately the one order of magnitude. The much CNT make up many path of the electron pass and interfere movement of electric charges. To improve conductivity of transparent conductive CNTs film, we are considering more uniform surface modification using 3-ATS and dispersion characteristics of CNTs on plastic substrates.

3. Conclusion

The transparent conductive CNTs film was formed by spraying of acid treated CNTs dispersed in IPA without any surfactant. We got a suitable adhesion of CNTs to desired substrate by surface treatment. The 3-ATS treatment of PET substrate improved the CNTs adhesion property to the substrate. The ink-jet printed patterning technique provided the optical transparent property improvement aside from conductivity of transparent conductive CNT composite films.

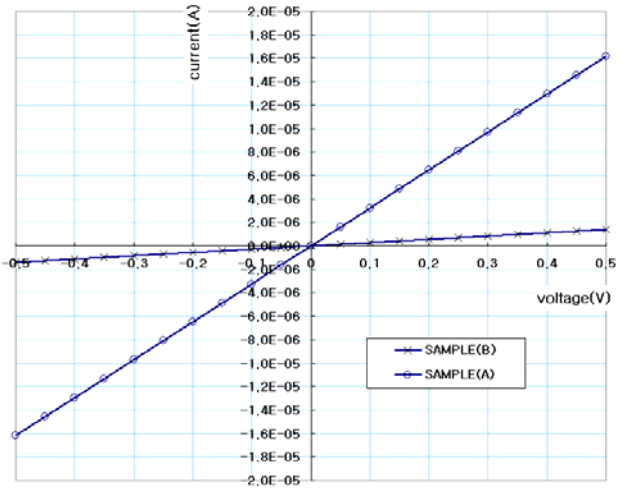

Figure 5. IV curves: SAMPLE(A); the plot of open circles is for "figure 2(A)" CNTs transparent film and SAMPLE(B); the plot of x-symbols is for "figure 4(D-1)" CNTs transparent film.

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5. References

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