# Controlling Adhesion Properties of SWCNT−PET Films Prepared by Wet Deposition

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ABSTRACT: Due to their unique properties, carbon nanotubes (CNTs) have been used as thin electrodes in plastic optoelectronic devices. In many applications, it is required that CNT electrodes be transparent, conductive and flexible, and most importantly, mechanically stable with good adhesion to the polymeric substrate. In this paper, we report on achieving SWCNT transparent and conductive films with excellent adhesion to polyethylene terephthalate, without any binder, by a simple and rapid post-treatment process. It was found that the best adhesion was achieved upon treating the films with acetic acid and formic acid, and with solutions containing 1−70% HNO_3. Morphological evaluations indicate the unique adhesion due to the SWCNT becoming partly embedded within the polymeric substrate during the post-treatment process, thus yielding flexible conductive films with high transparency.

KEYWORDS: carbon nanotubes film, transparent and flexible electrodes, adhesion, chemical treatment
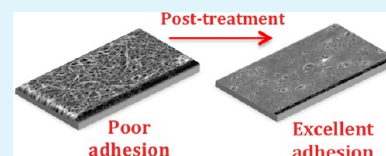
INTRODUCTION

Carbon nanotubes (CNTs) have been used as electrodes in optoelectronic devices, such as solar cells[1−3] and OLEDs,[4−6] in super capacitors[7] and sensors.[8,9] A good adhesion to the device substrate is essential to ensure constant electrode performance under friction, bending or in contact to liquids.[10,11]

Previous reports have suggested methods for preparing CNT transparent conductive films (TCF) with a desirable adhesion to the substrates. A common method for achieving a good adhesion of CNT to polymeric films is by using binders,[12−15] but the addition of either organic or inorganic binders, which are electrically insulating materials, increases remarkably the sheet resistance and may also decrease film transparency. Another approach to increase CNT adhesion is to deposit a thin metal layer between the substrate and the CNT film,[16,17] which compromises the optical properties of the film by decreasing the film transmittance and increasing haze. Pei et al.[18] suggested a method whereby films are prepared by electrophoretic deposition of single-walled (SW) CNTs on a metal electrode and then transferred to a polyethylene terephthalate (PET) substrate by hot pressing. Shim et al.[19] proposed the enhancement of adhesion between SWCNT film and polymer substrates by using microwave irradiation. Because SWCNTs can be heated selectivity under microwave irradiation, local heating and melting of the polymer surface occurs, so that the CNTs are welded to the polymer matrix.

Post-treatment by dipping the CNT-covered films in nitric acid has been widely used to improve conductivity.[14,20,21] The authors suggest that this treatment washes out the surfactant used to disperse the CNTs (usually an isolating material), thus increasing the conductivity. Other studies achieved improved conductivity by treatment with HNO_3 or/and $SOCl_4$, due to p-type doping of the CNT array.[22−24]

Rahy et al.[25] suggest that the presence of a surfactant located between the nanotubes prevents its adhesion to the polymer substrate. In their work, they concluded that the hydrophobic interaction, due to π−π stacking between the CNTs and the substrate, is the main factor for improving adhesion. On the other hand, Xu et al.[26] and Lee et al.[27] reported that mechanical interlocking between the SWCNTs and the substrate is the main reason for achieving good adhesion.

In this research, we report on a simple and rapid post-treatment process that is performed by dipping CNT films in various acids, which leads to partial embedding of the CNTs within the PET substrate, thus enabling the formation of transparent conductive films with excellent adhesion.

EXPERIMENTAL SECTION

Materials. Triton X100, HCl 37% and lactic acid were purchased from Sigma-Aldrich (Israel). Nitric acid (70%), ethanol absolute and acetone (technical grade) were purchased from Bio-Lab LTD (Israel). Formic acid (100%) and acetic acid (glacial) were purchased from Merck (Israel). Two types of CNTs were used in this work: SWCNT (carbon >90%, 0.7−1.4 nm diameter), from Sigma-Aldrich (Israel) and Hanos ASP-100F from Hanwha (Korea).

Methods. A SWCNT aqueous dispersion was prepared by dispersing 0.1 wt % SWCNTs in a 0.5 wt % Triton X100 aqueous solution (20 g) using a horn sonicator (Vibra-Cell, 750 W, Sonics & Materials Inc., USA) for 15 min, at 85% amplitude. The samples were cooled in an ice−water bath during the sonication process.

The CNT−PET films were prepared by wet coating polyethylene terephthalate films with the SWCNT dispersion. The coating was performed by draw-down (K Control Coater, R K Print-Coat Instruments Ltd., UK) at 3 m/min using a standard K101 bar coating with wire diameter of 0.64 mm, which gives a wet film thickness of 50

μm. Each film was formed by coating four layers of the dispersion and drying each layer at 100 °C.

The film's post-treatment was performed by dipping the SWCNT/PET film in a bath containing the treatment solution, at room temperature, for 5 min. Following dipping, the samples were dried at room temperature for 2 h.

The film characterization was performed by measuring the visible light transmittance (at 600 nm), using a Cary 100 UV−vis spectrophotometer (Varian, USA), the haze by using a Haze Gard+ (BYK-Gardener, Germany) and the sheet resistance by using a four-point probe Cascade Microtech (Beaverton, USA) coupled to an Extech milliohm meter (model 380562, Waltham, USA). Scanning electron microscopy (SEM) images were performed using the extra high resolution SEM Magellan 400, atomic force microscopy (AFM) using scanning probe microscope (Nanoscope Dimension 3100). X-ray photoelectron spectroscopy (XPS) analysis was performed by using Axis Ultra XPS (Kratos Analytical, UK) instrument.

The film height profile was measured by a mechanical profilometer Dektak 150 surface profiler (Veeco, USA). The PET films were coated by CNTs, and then areas of the coating were removed by a cotton swab, forming a height step, to enable differentiation between the PET film and the coated areas. The height profile was measured before and after HNO_3 treatment.

The adhesion properties of the film were evaluated by performing a peel-off tape test, using a Permacel 99 adhesive tape (Scotch, USA). The peeled off area was calculated by image analysis of the tape picture used in the test, using the software ImageJ.

Electroluminescent (EL) devices were fabricated by silk printing an EL paste composed of ZnS, and a dielectric paste of $BaTiO_3$ (MOBIChem, Israel) on top of the transparent electrode. The counter electrodes were prepared by inkjet printing a SWCNT formulation on top of the EL layer.

RESULTS

Initially, the films were prepared by coating with a liquid CNT dispersion that, after drying, yielded CNT films composed of SWCNT (16.6 wt %) and Triton X100 (83.3 wt %). The surfactant Triton X100 was required at a high concentration to disperse and stabilize the nanotubes in the dispersion. However, the high concentration of the surfactant is problematic, because it acts as an electrical insulator and, therefore, should be removed by washing.

To remove the surfactant, the PET−SWCNT films were dipped in solvents that were suitable for dissolving Triton X100, such as water, acetone and ethanol. Nitric acid solutions were also used (as suggested in previous reports for improving conductivity) and their effect was compared with that achieved by nonoxidizing acids, HCl, acetic acid and formic acid.

The light transmission (T%) of each film (before treatment) was measured at 600 nm, and was in the range of 75−76% for all the films. (The calculated concentration of the CNTs in the films was about 3 $\mu g/cm^2$.)

Each film was dipped in the treatment solution for 5 min and dried at room temperature and the light transmission was measured again. A slight increase in transmittance was observed after every treatment, probably because some contents (surfactant or SWCNTs) were washed off from the film during the post-treatment process.

A transparent and clear film should not only have a high light transmittancy but also a low haze value. The standard ASTM D-1003, which is the most widely used method in plastic electronics, defines "haze" as "that percentage of transmitted light, which in passing through the specimen, deviates from the incident beam by forward scattering more than 2.5" on the average.[28] The SWCNT films have, before treatment, a haze value of 6−6.5%, due to the presence of a large amount of

surfactant in the film. During post-treatment, the surfactant is washed away (at least partially) and the haze decreases, thus improving the optical properties of the films. The transmittance and haze measurements are summarized in Table 1.

Table 1. Optical Properties of SWCNTs before and after Treatment

washing solution		T (%) (at 600 nm)	haze (%)
none		75−76	6−6.5
H_2O		76.6 (±0.4)	4.8 (±0.2)
acetone		76.0 (±0.2)	3.3 (±0.4)
ethanol		77.1 (±0.1)	3.1 (±0.2)
HCl		75.8 (±0.2)	3.7 (±0.1)
formic acid		77.6 (±0.6)	2.7 (±0.4)
acetic acid		77.3 (±0.9)	2.5 (±0.6)
HNO_3	70%	76.8 (±0.8)	2.7 (±0.3)
	50%	76.0 (±0.6)	2.9 (±0.1)
	30%	75.2 (±0.8)	3.4 (±0.4)
	10%	76.7 (±0.7)	3.5 (±0.3)
	5%	76.7 (±0.6)	3.6 (±0.2)
	1%	77.9 (±0.9)	3.5 (±0.2)

The adhesion of SWCNT on PET substrates was evaluated after the various post-treatments by the peel-off method (tape test). This method is common in adhesion evaluation and gives qualitative results (pass or fail). In the case of SWCNT films, if the coating is peeled off the PET film, gray spots should be observed on the tape, after the test; if the film has good adhesion to the PET, the tape will be clean of SWCNT, remaining colorless after the test. As shown in Figure 1, the dark gray color indicates the presence of SWCNTs on the tape, meaning that the samples failed the tape test upon post-treatment with either water or ethanol (top row). The colorless tape indicates that the samples passed the tape test (bottom row) upon treatment with acids. The peeled off area (%) by the tape test could be estimated by image analysis, calculating the relative area of the tape covered by the gray spots of SWCNTs. A 100% peeled area means that the film was completely transferred to the tape (bad adhesion to the substrate), and an area of 0% means that the film remained on the substrate after the test (excellent adhesion).

In general, poor adhesion was observed in films treated with H_2O, acetone, ethanol and HCl, but surprisingly, very good adhesion was observed for films treated with formic acid, acetic acid and 70% HNO_3. We performed similar experiments with SWCNT films on polyethylene naphthalate (PEN) substrates, and the adhesion improvement was observed again.

The effect of HNO_3 solution concentration on the adhesion properties of SWCNT films was further evaluated. It was found that excellent adhesion was achieved when the films were treated with solutions containing 1−70% HNO_3. When films were treated with solutions containing <1% HNO_3, there was no adhesion. The adhesion test results are summarized in Table 2.

To understand the differences in the adhesion of films after each treatment, the films were observed before and after treatment by SEM (Figures 2 and 3) and AFM (Figure 4). A "carpet" of SWCNTs was observed in the film before treatment, together with a material between the nanotubes, which was probably the surfactant. After the films were treated with water, acetone, ethanol and HCl, no surfactant was observed. It can be understood that the surfactant was washed away, at least
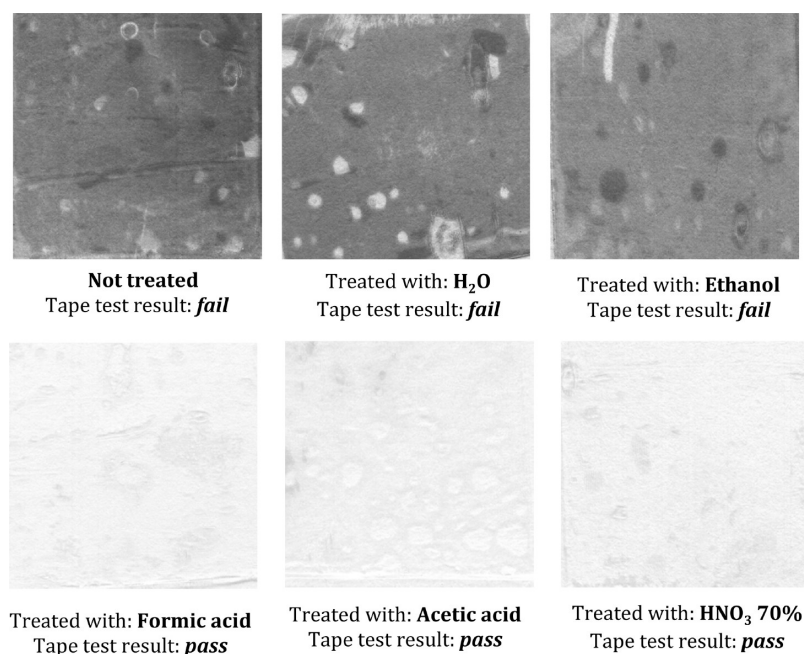
Not treated
Tape test result: *fail*

Treated with: H_2O
Tape test result: *fail*

Treated with: **Ethanol**
Tape test result: *fail*

Treated with: **Formic acid**
Tape test result: *pass*

Treated with: **Acetic acid**
Tape test result: *pass*

Treated with: HNO_3 **70%**
Tape test result: *pass*

Figure 1. Picture of Scotch tape after adhesion test evaluation prior and post treatment.

Table 2. Quantitative Adhesion Test of Nontreated and Post-Treated Films with HNO_3 at Various Concentrations

post-treatment		Scotch tape test	area peeled off by tape test (%)
not treated		fail	99.3
H_2O		fail	97.0
acetone		fail	99.4
ethanol		fail	97.3
HCl		fail	92.8
formic acid		pass	0.9
acetic acid		pass	0.6
HNO_3	70%	pass	0.0
	50%	pass	0.0
	30%	pass	0.0
	10%	pass	0.0
	5%	pass	0.0
	1%	pass	0.0
	0.5%	fail	94.6
	0.25%	fail	95.2

partially, from the nanotubes' surface, in accordance with the conclusion reached regarding the optical measurement before and after the post-treatment. In general, it should be noted that in all the samples, in which the SWCNTs could be clearly observed, the films had poor adhesion to the substrate, thus failing in the tape test.

A totally different morphology was observed in films that presented good adhesion to the substrate (samples treated with formic, acetic and nitric acid). In these samples, the SWCNT layer could hardly be seen, and seemed to be embedded within the PET film with only small areas of visible SWCNTs that stuck out of the film. Figure 3 shows a ripped SWCNT/PET film, where some units of SWCNTs can be seen going out from the thin CNT layer embedded in the PET.

A similar morphology was observed by AFM. Initially, SWCNTs can be seen in films before and after washing with water, acetone, ethanol and HCl. The SWCNTs are no longer seen after dipping in nitric, acetic and formic acids. To

determine whether the cause of the improved adhesion is as a result of changes that occur in the PET surface, PET films without SWCNTs were dipped in the same solutions and scanned by AFM. No visible change in surface morphology could be found. As control experiments, these substrates were coated with SWCNTs, without any additional post-treatment. The adhesion of CNTs in this case was poor, indicating that the adhesion improvement is not due chemicals modifications on the PET surface due to the dipping in acids. The adhesion improvement occurs only in cases were the SWCNTs are in contact with the polymer surface during the acid treatment process.

The film height profile was evaluated by scanning the uncoated and coated area by a mechanical profilometer. The height prior to HNO_3 treatment was about 60−150 nm. The same sample was treated with 70% HNO_3 (which improved the film adhesion) and scanned again. After the treatment, there were no significant differences of height of the bare PET film and the CNT covered area. This result indicates that most of the CNTs are embedded within the PET film, in agreement with the adhesion results. It should be noted that because the PET itself is not a flat substrate, there were large variations in the measurements, so we can report only on the trend of the profilometer results.

XPS analysis was performed for PET and SWCNT+PET films before and after treatments (Table 3). On the commercial PET without the SWCNT coating, the measurement revealed the presence of the following bonds: C—H (58.5%), C—O (24.8%) and C=O (13.2%). No significant changes were observed after dipping the PET in all the treatment solutions. This suggests that there were no chemical changes in the PET substrate during the post-treatment.

After the PET was coated with SWCNTs, the presence of the following bonds was observed: C—H (51.5%), C—O (46.5%) and COOH (2.4%). Because the C—C bond group (character-istic to CNTs) was not detected, it can be concluded that those chemical groups are related to the surfactant Triton X100, which is the main component of the dried film content (83.3 wt
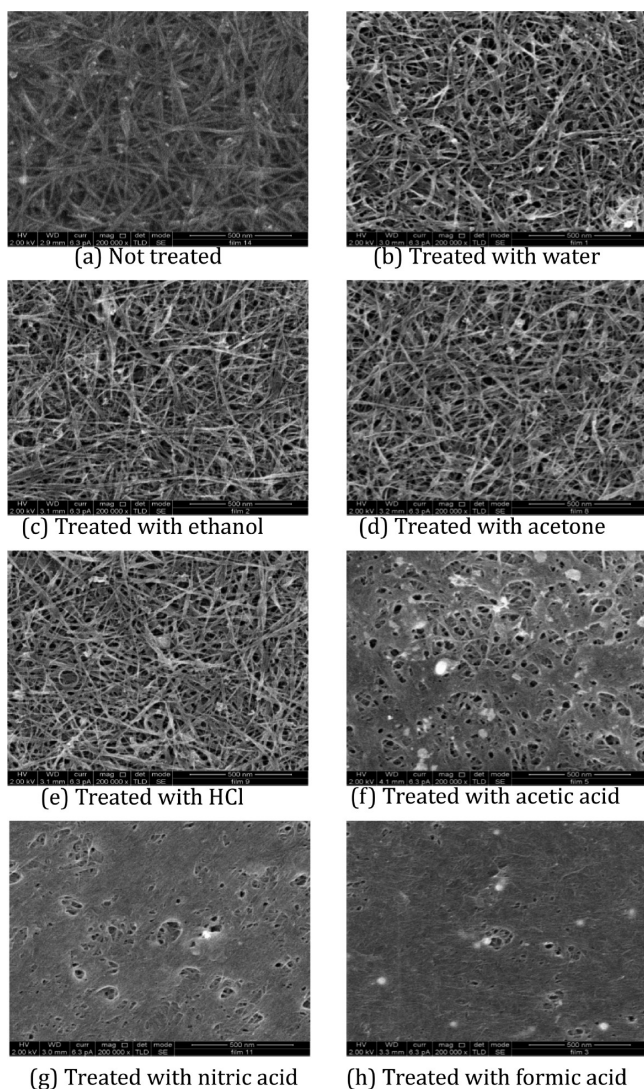
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(a) Not treated   (b) Treated with water

(c) Treated with ethanol   (d) Treated with acetone

(e) Treated with HCl   (f) Treated with acetic acid

(g) Treated with nitric acid   (h) Treated with formic acid

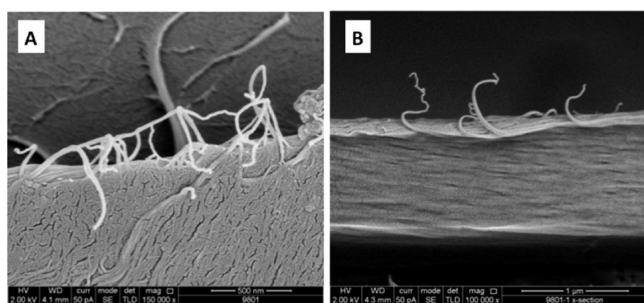**Figure 2.** SEM images of SWCNT films on PET, before (a) and after treatment (b–h).

Figure 3. Carbon nanotubes seen after ripping the SWCNT/PET film. (A) Lower part shows the SWCNT film embedded on PET, upper part shows PET after the removal of SWCNTs Layer by ripping. (B) Cross section of the SWCNT/PET film showing few SWCNTs going out from the CNT layer embedded in the PET matrix.

%). During the dispersion process, it is expected that the surfactant adsorb to the nanotubes surface, wrapping each tube separately.[29] After the films were treated with various solutions, C–C bonds were detected (27.2–32.5%). The presence of COOH groups increased (5.9–7.6%) whereas that of C–O (18.6–24.9%) and of C–H decreased (41.2–44.6%). These

changes in the surface chemical composition are due to the removal of the Triton X100 during post-treatment, as demonstrated in the results shown before.

The XPS analysis also proves that the adhesion improvement of the SWCNT film on the PET is not due to chemical modifications of the polymer surface caused by the post-treatment. Furthermore, it is clear that although hardly visible by SEM and AFM, the CNTs are present at the upper layer of the PET films, most probably embedded within that layer.

It was previously reported that oxidation of the CNT (forming –COOH groups on the surface) may increase the covalent bonding between the nanotubes and the polymer matrix in composites.[30,31] It should be noted that there were no significant changes on the SWCNTs' surface as a function of the post-treatment, especially regarding the –COOH groups. Therefore, the XPS analysis, the SEM images (showing that the SWCNT layer is embedded in the PET) and the mechanical profilometer scanning suggest that the improved adhesion is due to the penetration of the nanotubes into the polymer matrix. Furthermore, the penetration is probably caused by physical changes in the polymer, such as a swelling or a plasticizing effect caused by the formic, acetic or nitric acid.

In addition to the adhesion improvement, the electrical properties of the films can also be controlled by post-treatment. Although SWCNTs have excellent electrical conductivity, the surfactants (such as Triton X100) have very high resistivity and, therefore, it should be removed. Before any post-treatment, the sheet resistance is above 90 kΩ/□.

After all post-treatments performed in this study, in general, it was found that the sheet resistance decreased, but particularly with HNO_3. Previous studies reported on the effect of a 70% HNO_3 solution on CNTs' conductivity due to a doping process. Because we found that a good adhesion can be achieved after treating the films with low concentration of (from 1%) HNO_3, we examined the effect of those treatments on the film conductivity.

We found that varying the HNO_3 concentration enables us to control the conductivity of the films. The sheet resistance decreases to about 1.1 kΩ/□ after treatment with 10% HNO_3 solution, and continues to decrease as long as the concentration of HNO_3 is increased, reaching a low value of 190 Ω/□ when using a solution of 70% HNO_3. Because treatment using a solution of 90% HNO_3 completely damages the PET substrate, the resistance of the sampled sheets could not be measured. The resistivity of 190 Ω/□ is not the best reported value; however, this can be further improved by the proper selection of the CNT type and other formulation parameters, which is not the main focus of the present research.

It should be noted that treatment with other solutions that improved the adhesion (acetic acid and formic acid) yielded much higher resistance values than HNO_3, indicating the explicit role of the latter. The effect of HNO_3 concentration on improving film conductivity is demonstrated in Figure 5.

It is interesting to note that we applied the same post-treatment process with the acids for a variety of CNTs and in all cases, we found that excellent adhesion was obtained, while the CNTs became part of the upper layer of the polymeric substrate.

The transparent conductive SWCNT films were used as electrodes in flexible electroluminescent (EL) devices (Figure 6). This type of device is composed of two electrodes, one of them is transparent, and between them is an electroluminescent paste, which emits light when voltage is applied. We found that
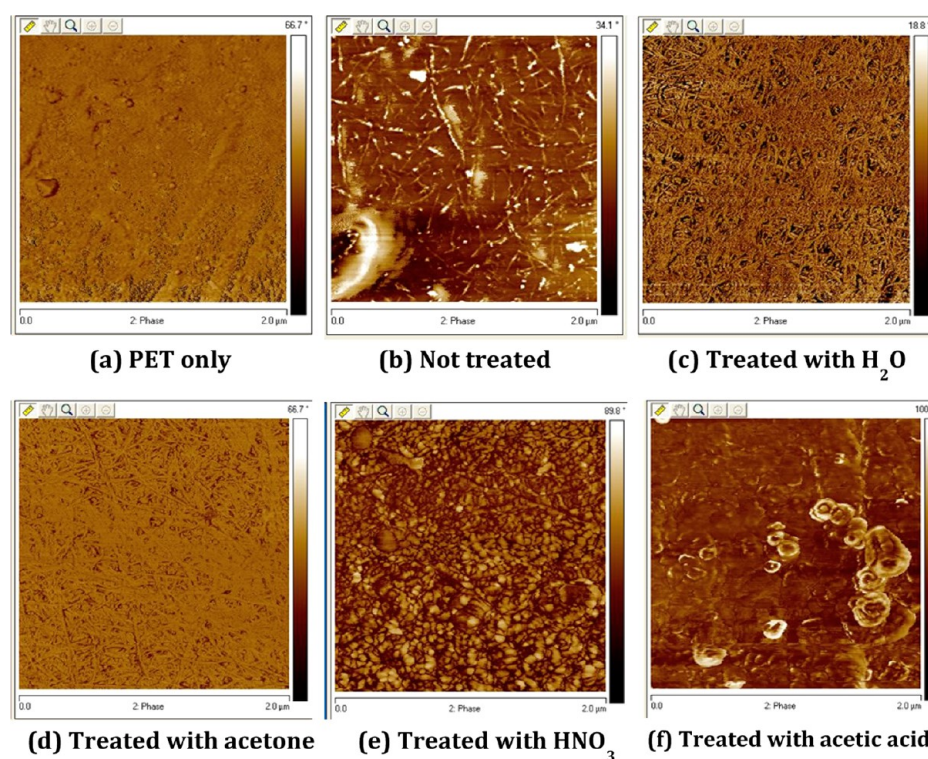
Figure 4. AFM scans of PET substrate (a) and SWCNT films on PET, before (b) and after treatment (c–f).

Table 3. XPS Analysis of PET and PET-SWCNTs Films before and after Treatment

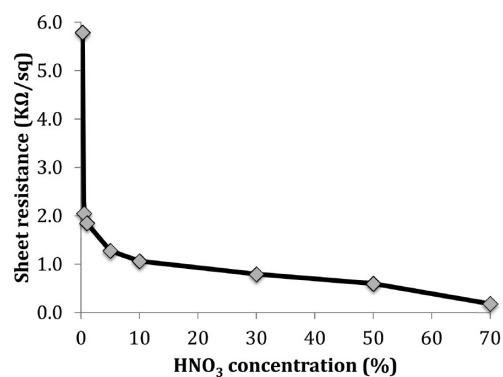|	PET only			SWCNT film on PET			
	peak area %			peak area %			
post-treatment	C—H	C—O	C=O	C—H	C—O	COOH	C—C
none	58.5	24.8	13.2	51.5	46.5	2.4	
H_2O	58.5	25.8	15.6	41.2	24.9	5.9	28.0
acetone	58.7	26.1	15.2	42.4	19.5	6.5	31.9
ethanol	58.5	26.6	14.9	43.1	19.1	6.9	30.9
HCl	59.5	26.5	14.0	42.5	22.8	7.6	27.2
formic acid	58.9	24.2	16.9	42.5	18.8	6.2	32.5
acetic acid	56.8	26.5	16.6	44.6	20.9	6.1	28.4
HNO_3 70%	55.5	28.4	16.4	44.1	18.6	6.4	30.9

Figure 5. Effect of HNO_3 concentration on CNT film sheet resistance.

the films formed, which had a sheet resistance lower than 1 kΩ/□, were suitable for fabricating the EL devices. The counter electrode was prepared by inkjet printing the SWCNT formulation on top of the electroluminescent layer.

The excellent adhesion of the films enabled good mechanical stability, which is essential to ensure the EL performance under bending. The flexibility of the films was tested by bending it for at least 25 times at an angle of 180°. It was found that after bending, the SWCNT film sheet resistance remains constant, as well as the EL performance.

■ CONCLUSIONS

In conclusion, we found that it is possible to improve the optical, electrical and adhesion properties of SWCNT transparent films on PET by a simple and rapid post-treatment that entails dipping the films in various solutions, at room temperature. It was observed that the light transmittance of the films increased and the haze % decreased after the post-treatments, mainly due to the removal of the surfactant from the film. The removal of the surfactant also led to improved electrical properties: the sheet resistance decreased after all the treatments, but particularly after treating the films with HNO_3. It was observed that the decrease in sheet resistance depended on HNO_3 concentration, reaching a minimum when using 70% HNO_3. This results from an additional dopping process, as reported earlier.[22−24] The adhesion of the SWCNTs on the PET was extremely improved after treating the films with HNO_3 (1−70%), acetic acid and formic acid. It was also concluded that in these films, the SWCNTs were embedded within the PET substrate, probably due to physical changes in the film (swelling or plasticizing effect) caused by the treatment solutions. The results suggest that the penetration of CNTs into the polymer accompanied by mechanical interlocking between the SWCNT and polymer chains is the main factor for the excellent adhesion of the PET surface.
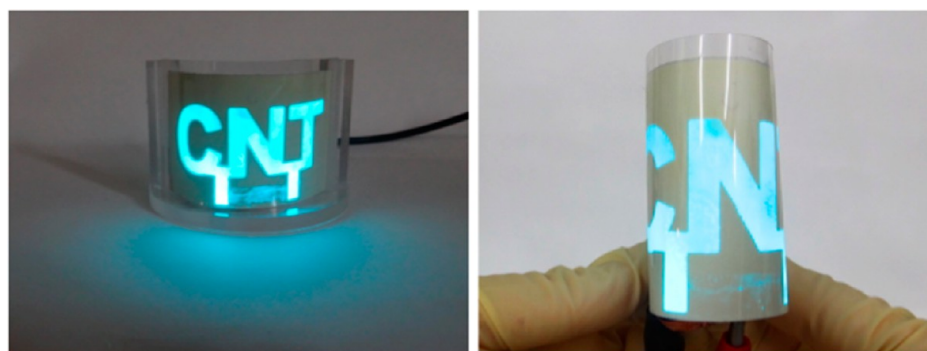
Figure 6. Flexible electroluminescent device formed by SWCNT electrodes. The performance of the device remains unchanged after a bending of 180°.

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Notes

The authors declare no competing financial interest.

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