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Base and Acid Treatment of SWCNT-RNA Transparent Conductive Films

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ABSTRACT RNA was used to exfoliate single-walled carbon nanotubes (SWCNTs) in aqueous solution, and the ratio of it was optimized to obtain the best dispersion state. The obtained homogeneous SWCNT solution with small bundle size was used to prepare flexible transparent conductive films by filtration method. Sodium hydroxide treatment combining short-time acid treatment was used to remove the RNA molecules. After treatment, the sheet resistance of the films decreased significantly, while the change on the transmittance was negligible. Besides, the polyethylene terephthalate substrate would not turn brittle through this treatment process. Flexible films with outstanding performance (190 Ω/sq, 85%) and good stability were obtained after treatment. X-ray photoelectron spectroscopy and scanning electron microscope were used to analyze the role of base and acid treatment in detail.

KEYWORDS: SWCNTs · RNA · thin films · post treatment · dispersion

Transparent conductive films (TCFs) have been widely used in electronic devices, such as transparent electrodes,[1] touch screens,[2] liquid crystal displays (LCDs),[3] organic light-emitting diodes (OLEDs),[4] and photovoltaics.[5] TCFs made from indium tin oxide (ITO) monopolized the market in last several decades because of its excellent conductivity and transparency. Unfortunately, some disadvantages of ITO loomed these few years. First, the price of indium has soared over the past decade, which increased the cost of ITO significantly. Second, brittleness of ITO limited its applications in flexible devices, such as e-paper. It was reported that strains above ~1% would result in irreversible loss of the conductivity of ITO.[6] Carbon nanotube (CNT) is an ideal candidate to replace ITO due to its outstanding flexibility and unique electrical property. A lot of research has been done on transparent conductive CNT films in recent years. Some research focused on the influence of CNT types. Zhang *et al* prepared thin films from different kinds of CNTs and revealed that films of arc discharge nanotubes were overwhelmingly better than films prepared with high-pressure carbon monoxide (HiPCO) tubes.[7] The influence of nanotube chirality was also investigated.[8,9] Post treatment became another research focus in the past few years. Nitric acid[10] and thionyl chloride ($SOCl_2$)[11] have been used to dope CNT films to enhance their conductivity. Adding conductive polymers also gained interest of worldwide scientists. De *et al* have made CNT films with high conductivity ($>10^5$ S/m) by adding single-walled carbon nanotubes (SWCNTs) into conductive polymers, and the sheet resistance of the films kept stable after over 100 cycles of bending.[12] In addition, highly automated and scalable methods were pursued by researchers. Dan *et al* presented a highly scalable and continuous method for making uniform CNT thin films.[13]

Various methods have been developed to fabricate CNT films, including bar coating,[13] vacuum filtration,[14] spray coating,[15] spin coating,[16] dip coating[17] and Langmuir−Blodgett deposition.[18] No matter which method you choose to fabricate CNT thin films, the first crucial step is to obtain homogeneous and stable CNT solutions with small bundle size. However, most commercial SWCNTs aggregate into thick bundles due to their high surface energy and strong van der Waals force between them. Several strategies have been developed to debundle SWCNTs, including covalent and noncovalent modification. Covalent modification will induce some defects on the side walls and decrease the conductance of SWCNTs. On the contrary, noncovalent wrapping is more efficient to obtain debundled SWCNTs solutions with few damages. Although large numbers of dispersants have been used to exfoliate CNTs, not all of them are suitable to prepare trans-

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parent conductive films (TCFs). The most common dispersants used in TCFs are anionic surfactants, including sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS). They are preferable dispersants because nanotubes can be highly exfoliated by them at rather high concentrations.[19] Besides, they nearly have no absorption over the visible spectrum region. However, they are not without disadvantages. Large amounts of them are needed to exfoliate nanotubes into thin bundles; usually the critical micelle concentration (CMC) value should be reached.[20] Their residue will increase the sheet resistance of nanotube films significantly since they are nonconductive.

In recent years, a lot of research has been done on the dispersion of CNTs with biomolecules such as DNA and RNA.[21−24] There are a number of advantages using them as dispersants. First, they can coat, separate, and solubilize CNTs more effectively with their phosphate backbones interacting with water and many bases binding to CNTs.[25] DNA wrapped around CNTs helically, and there were strong $\pi-\pi$ interactions between them.[26] Charges were transferred from the bases of DNA to CNTs leading to the change of their electron structures and electrical property.[27] An 1 mg amount of DNA could disperse an equal amount of as-produced HiPCO CNT in 1 mL water, yielding 0.2 to 0.4 mg/mL CNT solution after removal of nonsoluble material by centrifugation. Such a CNT solution could be further concentrated by 10-fold to give a concentration as high as 4 mg/mL.[22] Jeynes's research disclosed that total cellular RNA showed better dispersion ability than dT(30), which was the most effective oligonucleotide dispersant in previous reports.[24] Second, the amount of DNA needed to exfoliate CNTs into thin bundles was much less than common surfactants, such as sodium dodecyl sulfate (SDS). In Zheng's work, the weight ratio between SWCNTs and DNA was 1:1,[22] while the dosage of RNA in Jeynes's work was lower, only half of the amount of the nanotubes.[24] By contrast, 10-fold of SDS was needed to exfoliate SWCNTs efficiently.[15,28] A high dosage of dispersant is not preferred since they are nonconductive, and their residue will decrease the conductivity of the films significantly. Third, they have little absorption over the visible range and will not decrease the transmittance of CNT films. Last but not least, as biomolecules, they are easily degraded and removed by acid, base, or appropriate enzyme. Jeynes *et al* have used RNA to disperse CNTs and digested them by RNase effectively.[24]

In this work, RNA was used to disperse SWCNTs. The influence of the ratio of SWCNTs to RNA and the concentration of sodium acetate were investigated systematically. Flexible SWCNT thin films were made and post-treated by sodium hydroxide solution for the first time. Although nitric acid was effective to remove dispersants, they induced p-doping of CNTs, which will lead to instability of the films.[29] Besides, PET substrates will turn brittle after long time acid treatment. These problems were solved perfectly by combining base and short-time acid treatments.

RESULTS AND DISCUSSION

Dispersion of SWCNTs. In order to obtain the optimal dispersion state, different amounts of RNA were added to exfoliate SWCNTs. The obtained ink-like solutions were characterized by transmission electron microscopy (TEM). Comparing Figure 1a−c, we can see that when the ratio of RNA was high, SWCNTs aggregated into big bundles rather than exfoliating into individual ones. This may be attributed to the adhesion effect of the excess RNA. When the ratio of RNA was high, some of them wrapped around CNTs to exfoliate them into thin bundles, while the excess RNA aggregated and adhered thin bundles into thick ones. The dispersion state was apparently improved when the ratio of SWCNT:RNA was increased to 2. Thick bundles exfoliated into thin ones, and the concentration of SWCNTs also increased greatly, as seen from the absorption spectra (Figure 2). However, there was still some excess RNA. They aggregated and connected SWCNT bundles leading to the inhomogeneity of the dispersion (Figure 1b). When the ratio of RNA decreased further, excess RNA disappeared. However, the concentration of SWCNTs after centrifugation decreased a lot compared to the previous ratio (Figure 2), and the bundles turned thicker. Sodium acetate was added to improve the dissolution of RNA. ComparingFigure 1b with d, when the concentration of NaAc was increased to 0.1 M, RNA dissolved more uniformly and fewer of them aggregated. Therefore, fewer SWCNT bundles were connected together, and most of them kept thin bundles. Besides, the SWCNTs solution turned to become more homogeneous. Although the concentration of SWCNTs decreased a little with the increase of NaAc, it was beneficial for film preparation considering the homogeneity and smaller bundle size of the SWCNT solution. According to the above investigation, we found that the best dispersion state can be obtained when the ratio of SWCNT:RNA is 2 with the concentration of NaAc as 0.1 M.

Preparation of SWCNT-RNA Films and Their Post Treatment. SWCNT solution was prepared under the optimal condition and used to prepare thin films with a vacuum filtration method. A four-point probe resistivity meter was used to measure the sheet resistance of the films. Five points were measured, and the mean values were used to represent the sheet resistance of the films. The relative standard deviation was used to characterize the uniformity of the films, and it was below 10% in this work. Figure 3a disclosed that the performance of SWCNT-RNA film was very close to the criteria of touch screen ($<$500 Ω/sq, 85% T) even without any post treatment. This

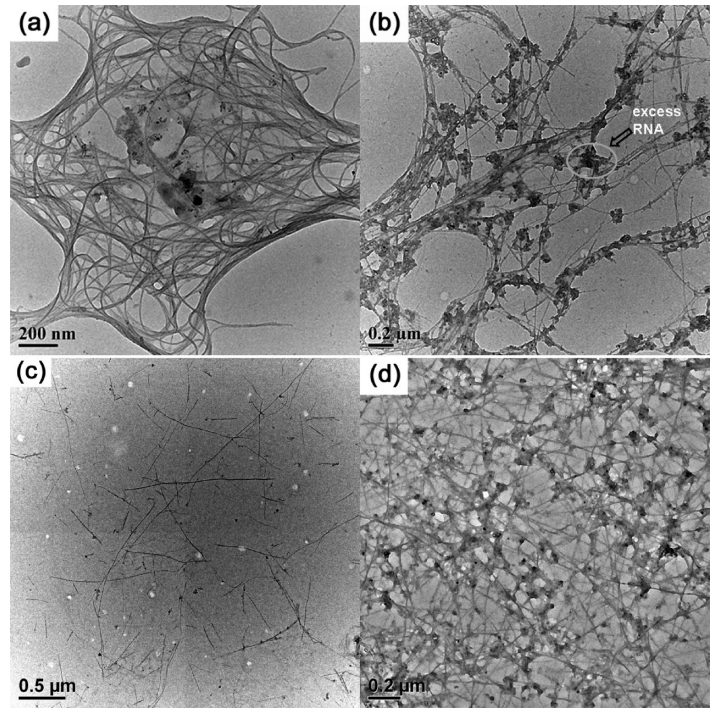

Figure 1. TEM images of SWCNT solutions dispersed by RNA: (a) SWCNT:RNA = 1:1, 0.03 M NaAc; (b) SWCNT:RNA = 2:1, 0.03 M NaAc; (c) SWCNT:RNA = 4:1, 0.03 M NaAc; and (d) SWCNT:RNA = 2:1, 0.1 M NaAc.

was attributed to the excellent dispersion state. Acid treatment was effective to remove dispersants according to previous reports[15] and our previous work. However, long-time acid treatment would induce doping which would lead to the instability of the films.[29] Besides, PET substrates would turn brittle after long-time acid treatment. Fortunately, our dispersant RNA could also be degraded and removed by base solution. As seen from Figure 3a, the sheet resistance of SWCNT-RNA films decreased a lot after treatment with sodium hydroxide solution (5 wt %) for 1 h. Sodium hydroxide solutions with concentrations between 1 and 30 wt % were all effective to remove RNA. Films would breach or peel off when treated by sodium hydroxide solutions with a concentration higher than 30%. The influence of base treatment time on the performance of the films was shown in Figure 3b. Transmittance of the two films used in Figure 3b was 95% and 96%, which meant

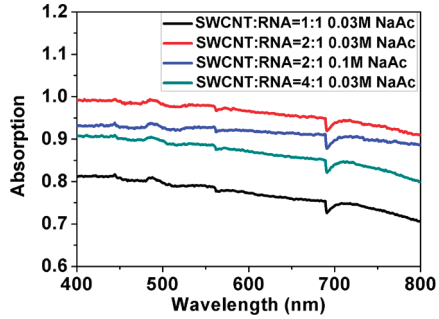

Figure 2. Absorption spectra of SWCNT solutions dispersed by RNA with different SWCNT:RNA ratio and different concentration of NaAc.

the difference between the thicknesses of the two films was negligible. The same thickness should be guaranteed since it influenced the degradation of RNA greatly. The sheet resistance decreased significantly in the first several minutes when treated with 1.25 wt % NaOH solution. Then, it decreased slowly until the second hour. This indicates that dispersants covered on the surface of the film was easy to remove, while interior dispersants took a long time to be removed. The sheet resistance decreased more in the first several minutes when treated with 5 wt % NaOH solution, and less time was needed to achieve the lowest value. The sheet resistance increased slightly when the treatment time prolonged to 2 h. This may because P3 SWCNTs, which were highly p-doped in the purification process, were slightly dedoped by base treatment.[30] The sheet resistance decreased less after 1 h base treatment when the films became thicker, as seen from Figure 3c. For thick films, there were more interior dispersants, which meant a longer time was needed to remove the dispersants completely.

After base treatment, short-time acid treatment was also used to further improve the performance of SWCNT films. Figure 3a showed that the sheet resistance decreased a lot after base treatment, and it decreased further after treatment with nitric acid for 10 min. Sheet resistance of 190 Ω/sq at the transmittance of 85% was obtained. Figure 3d showed that the change of transmittance was negligible after base and further acid treatments. The stability of SWCNT-RNA films after treatment was investigated. They were rather

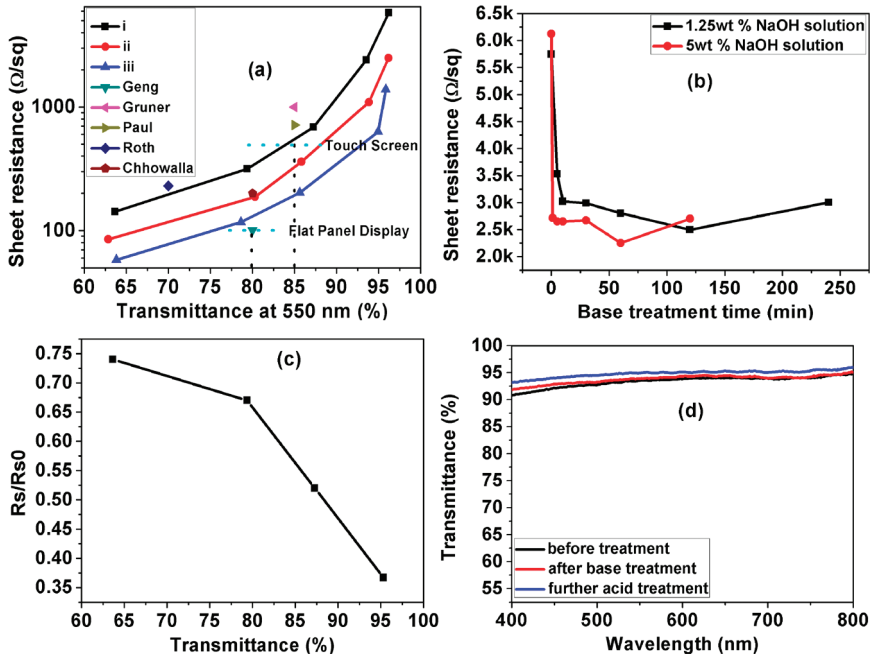

Figure 3. (a) Sheet resistance versus transmittance at 550 nm before and after treatment with previously reported values for comparison: (i) as prepared SWCNT-RNA films; (ii) NaOH treatment for 1 h; and (iii) further HNO_3 treatment for 10 min. (b) The sheet resistance change of SWCNT-RNA films with base treatment time. (c) The sheet resistance change of SWCNT-RNA films with different thickness after 5% NaOH solution treatment for 1 h. The sheet resistance was normalized by the initial sheet resistance. (d) The change of the transmittance before and after treatment.

stable; the sheet resistance deviation was below 8% after one month. This was negligible considering the deviation induced by measurement.

XPS analysis was used to investigate the role of base and acid treatments intensively. Figure 4a disclosed that the main peak of C1s of reference films appeared at 284.5 eV, which is identified as a sp^2 carbon.[31] The broad band at higher binding energy corresponds to −COOH groups which existed in P3 SWCNTs. The signal of −COOH group reduced a lot when RNA was added due to its coverage. It appeared again after treatment by 5% NaOH solution for 1 h, which indicated the removal of RNA molecules. The analysis of an O peak showed the same trends. For pure SWCNT film, the O signal originated mainly from −COOH group seen from Figure 4b. The O1s peak up-shifted to 532.85 eV, which was marked as a C−O group after introducing RNA. After base treatment, it downshifted back, testifying the removal of RNA. Phosphorus from the phosphodiester bond represented the existence of RNA

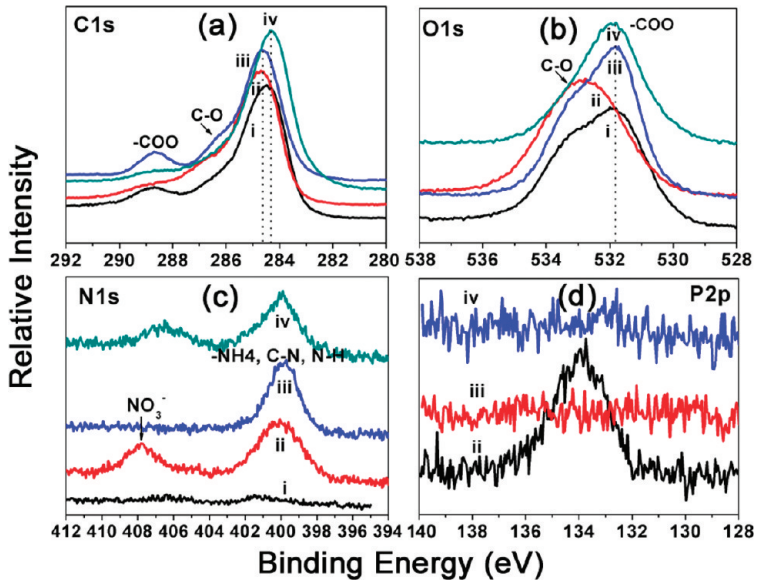

Figure 4. XPS analysis of SWCNT-DNA films before and after acid treatment. Spectrum: (i) SWCNT film without any dispersant (reference film); (ii) SWCNT-RNA film; (iii) SWCNT-RNA film after base treatment for 1 h; and (iv) SWCNT-RNA film after further acid treatment for 10 min.

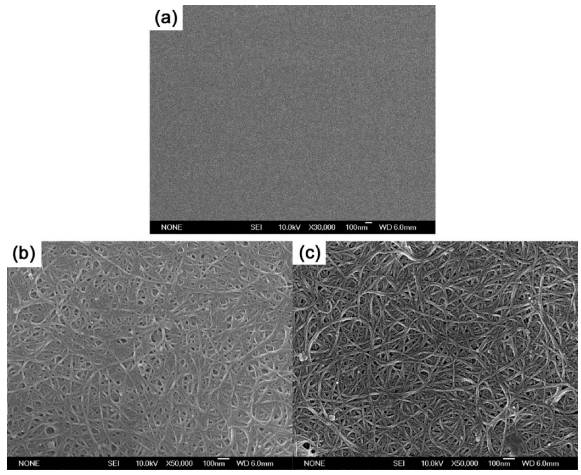

Figure 5. SEM images of SWCNT-RNA films before and after treatment: (a) before treatment; (b) after treatment with 5% NaOH solution for 1 h; and (c) after further treatment with 14 M nitric acid for 10 min.

backbones. For SWCNT-RNA films, most of the RNA backbones were removed after base treatment since no phosphorus could be detected. However, a lot of −NH/C−N groups still existed signifying the residue of RNA bases. This may owe to strong π−π interactions between the C═N/C═C double bonds of RNA and SWCNTs.[26,32] The amount of −NH/C−N groups decreased after nitric acid treatment, verifying the further removal of the bases.

The shifts of C1s peak position can be used to characterize the interaction between SWCNTs and dispersants and the doping effect of HNO_3 on CNTs.[33] The C1s peak would shift toward a higher binding energy if CNTs accepted electrons from surroundings and *vise versa*. As seen from Figure 4a, a 0.3 eV upshift of C1s peak occurred when RNA was introduced, testifying the electron transfer from RNA to CNTs. After base treatment, the C1s peak was slightly down shifted (0.1 eV), indicating the removal of RNA. Since a lot of bases still resided on the wall of nanotubes and donated electrons to them, the shift of C1s peak was not apparent. The C1s peak shifted back to 284.33 eV after treatment with nitric acid for 10 min, owing to further removal of RNA and the p-doping effect induced by nitric acid. This was deduced from Figure 4c which showed that the area of −NH peak decreased and the NO_3^- peak increased.

The morphology evolution of SWCNT-RNA films before and after treatment was shown in Figure 5. Before treatment, the surface of the film was covered by a layer of dispersants, and CNTs could not be observed. After treatment with NaOH solution for 1 h, RNA molecules on the surface were removed, and clear SWCNT networks appeared. Comparing Figure 5b to c, we could see that SWCNT networks were clearer after acid treatment, testifying further removal of dispersants.

According to the above analysis and the properties of RNA, the removal mechanism of RNA was deduced, and the schematic diagram was shown in Figure 6.

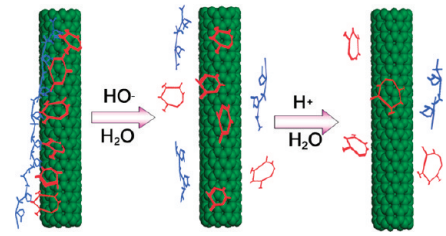

Figure 6. Schematic diagram of the removal mechanism of RNA; blue, RNA backbones; red, RNA bases; and green, nanotubes.

When immersed in NaOH solution both phosphodiester and glycosidic bonds were hydrolyzed. Hydrolysis of the phosphodiester bond would lead to the rupture of RNA backbones into short fragments, while hydrolysis of the glycosidic bond would cut the connection between the backbones and bases. Therefore, in the base treatment process, RNA backbones were cut into short chains and separated from the bases. These short RNA backbones were easily removed since there were no connections between them and the nanotubes. However, due to the π−π interactions between the C═N/C═C double bonds of RNA and SWCNTs, a lot of bases still resided on the walls of nanotubes, which was deduced from the remaining −NH peaks in XPS spectra. After further short-time acid treatment, more bases were removed, although the mechanism was still not clear. A weak p-doping effect was also induced by nitric acid, which was verified by the shift of C1s peak position and the enhancement of NO_3^- peak. Fortunately, this did not lead to the instability of our films.

CONCLUSION

RNA was used to exfoliate single-walled carbon nanotubes (SWCNTs) in aqueous solution, and the ratio of it was optimized. SWCNT solutions with smaller bundle size and higher concentration were obtained when the ratio of SWCNT:RNA is 2. A more homogeneous SWCNT solution was obtained after adding sodium acetate since it can improve the dissolution of RNA. The obtained homogeneous SWCNT solution was used to prepare flexible transparent conductive films by filtration method. Films with good performance were obtained even without any post-treatment due to the excellent exfoliation of SWCNTs. Sodium hydroxide solution was used to remove dispersants for the first time. Sodium hydroxide solutions with a concentration between 1 and 30 wt % were all effective in removing RNA, and the treatment effect was influenced by the concentration of NaOH solution, treatment time, and the thickness of the films. Most of RNA molecules were removed after treatment according to XPS analysis and SEM images, and the sheet resistance decreased a lot. Short-time acid treatment was used to remove RNA molecules further. After treatment, flexible films with outstanding performance (190 Ω/sq, 85%) and

good stability were obtained. Base treatment combining short-time acid treatment could remove RNA molecules efficiently as well as retaining the flexibility of PET substrates and the stability of the films. It is of great significance in preparing flexible CNT films with high conductivity and transmittance.

EXPERIMENTAL METHODS

Chemicals. The P3 SWCNTs purchased from Carbon Solutions Inc. were synthesized by an arc-discharge method and purified with nitric acid. This kind of nanotube contains 1.5−3.0 atomic % carboxyl groups. RNA (torula yeast, type VI) was purchased from Sigma Chemicals.

Dispersion of SWCNTs. RNA was dissolved in 0.03 or 0.1 M NaAc aqueous solution. Then, P3 SWCNTs were added and bath sonicated for 2 h. The weight ratio of CNTs:RNA is between 1:1 and 4:1. The obtained dark solution was centrifuged at 13 000 rpm for 30 min. The supernatant was carefully collected and subjected to another round of 30 min centrifugation at 13 000 rpm.

Film Fabrication. A vacuum filtration method was used to prepare transparent conductive films of SWCNTs. The above supernatant was diluted with water by 20 fold. Then 10−60 mL solutions were filtrated through a 220 nm Millipore ester membrane to prepare films. After filtration, the filter membranes were then transferred onto PET substrates, dried in air at 90 °C for 1 h, and then dipped in acetone for 30 min to dissolve the filtration membrane, leaving SWCNTs thin films on the PET substrates. The obtained films were finally dried at 90 °C for 2 h.

Post Treatment. The films were immersed in a sodium hydroxide solution for a certain time and then rinsed with water. Then the films were dried at 60 °C for 3 h, and their resistance was measured. After that, the films were further treated with 14 M nitric acid for 10 min and then rinsed with water. The films were finally dried at 60 °C for 3 h.

Characterization. The dispersion states of SWCNTs were characterized by TEM (JEM-2100F, JEOL, Tokyo, Japan). SEM images of SWCNT films were taken on a field emission scanning electron microscope (FESEM, JEOL, JSM-6700F). The transmittance at 550 nm of the films was measured *via* a UV−vis spectrometer (Lambda 950, Perkin-Elmer, Shelton, USA). A four-point probe resistivity meter (Loresta EP MCP-T360, Mitsubishi Chemical, Japan) was used to measure the sheet resistance of the films. X-ray photoelectron spectra (XPS) analysis was conducted using the Mg Kα (1253.6 eV) monochromatic X-ray source (Axis Ultra DLD, Kratos).

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