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Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films

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Despite recent efforts for fabricating flexible transparent conducting films (TCFs) with low resistance and high transmittance, several obstacles to meet the requirement of flexible displays still remain. Filtration method is a useful tool to control the film thickness but limited to the filter size, which is a drawback for large size applications.[1−4] The spray coating method is a robust approach for large-size and uniform films, but the inherent sparse density increases the resistivity of film.[5] In this Communication, a spray method was introduced to fabricate TCFs on polyethylene terephthalate (PET) films using sodium dodecyl sulfate (SDS)-dispersed single-walled carbon nanotubes (SWCNTs). These films were further immersed in various acids. Excellent conductivity was obtained with a negligible change in the transmittance in the visible range. This enhancement was attributed to the removal of remaining SDS and the subsequent densified film formation to improve the cross-junction resistance between SWCNT networks and enhanced metallicity of SWCNTs, whereas the chemical doping effect was negligible unlike that previously reported on bucky paper.[8]

The SWCNTs synthesized by the arc discharge method (Iljin Nanotechnology, Inc.) were used to fabricate TCFs by a spray method. The SWCNT powder was dispersed with SDS in deionized water and sonicated, followed by the centrifugation. The SWCNT supernatant solution was then sprayed on PET film followed by several rinsings in water to remove the remaining SDS (see experimental procedures in Supporting Infromation S1). Figure 1a shows a typical sheet resistance−transmittance curve (open-circle line) in a wide range of film thicknesses in comparison with the previously reported values.[1−7] The film conductivity increased with increasing film thickness which was measured by atomic force microscopy (AFM) at step edges and was saturated to about 1500 S/cm at a thickness of about 50 nm (open-square line in Figure 1b). Although our results met the requirement of touch screen (TS: 500 Ω/sq, 85% T) for practical applications, the condition, for instance, for transparent conducting electrodes (50 Ω/sq, 85% T) was still not reached. The film performance strongly relies on the material qualities such as purity, diameter, defects, metallicity, and the degree of dispersion.[9] Nevertheless, this approach provides a systematic way of fabricating films with reasonable film performance compared to other related works. To improve the conductivity of film, the film was simply immersed in various acids. Several changes were observed. The sheet resistance with 12 M of HNO_3 treatment for 60 min was significantly reduced by a factor of about 2.5 times (Figure S1), while the changes in the transmittance were negligible in the visible region (Figure S2). The sheet resistances of ∼ 40 and 70 Ω/sq at the corresponding transmittances of 70 and 80% were obtained in this case (solid-circle line in Figure 1a). The low sheet resistance can meet the criteria of TCFs that may replace the conventional ITO with high flexibility for flat panel displays (FPD). The film thicknesses were reduced by about one-fourth of the pristine film owing to the removal of bulky SDS. Those yielded an enhancement in the conductivity by a factor of ∼4 times (solid-star line shown in Figure 1b, open-circle dashed line for comparison by presuming no change in the thickness). The conductivity at large thickness reached 5500 S/cm. This value is much larger than 960 S/cm of $SOCl_2$ treated bucky paper[10] and ∼2000 S/cm of $SOCl_2$-treated TCFs[2] and comparable to that prepared by filtration method.[1] The surface roughness (∼9 nm from AFM) was also improved by wetting some protruded nanotubes, as shown from the field-emission scanning electron microscopy (FESEM) images in Figure 1c,d. Similar effects were observed in the case of sulfuric acid treatment.

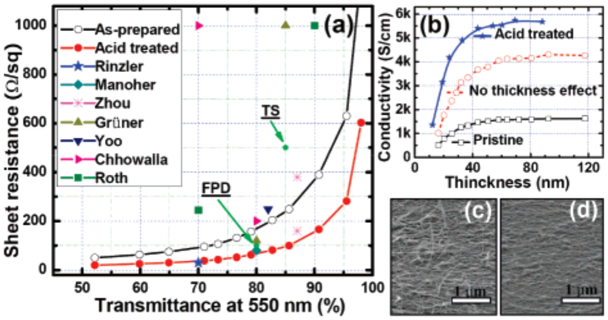

Figure 1. (a) Sheet resistance versus transmittance at 550 nm before (open-circle) and after (solid-circle) nitric acid treatment with previously reported values for comparison and (b) the corresponding conductivity as a function of film thickness before and after acid treatment. SEM images of (c) before and (d) after acid treatment, taken at a viewing angle of 60°.

To understand the effect of acid treatment, we present X-ray photoelectron spectroscopy (XPS) spectra in Figure 2. The peak position in C1s was ∼0.1 eV downshift by H_2SO_4 and no obvious shift by HNO_3 (inset), which is not so prominent compared to 0.5 and 0.2 eV of H_2SO_4- and HNO_3-treated[8] and 0.40 eV downshift of $SOCl_2$-treated[10] bucky paper. The development of oxygen-related peaks (inset) was not appreciable for both nitric and sulfuric acid-treated samples. NO-related peaks were developed with nitric acid treatment. What is more intriguing is the removal of sodium content and the SO_4^{2-} peak particularly in the nitric acid-treated sample. This ensures that the SDS was removed from the nanotube surface. Similar behavior was also observed in the sulfuric acid-treated sample except for an additional addition of SO_4^{2-} group after SDS removal (Figure S3). Our XPS analysis suggests that the main origin of the enhancement in conductivity is not the doping effect but the removal of insulating SDS in SWCNT networks and the subsequent densified film density. This is in good contrast with the previous

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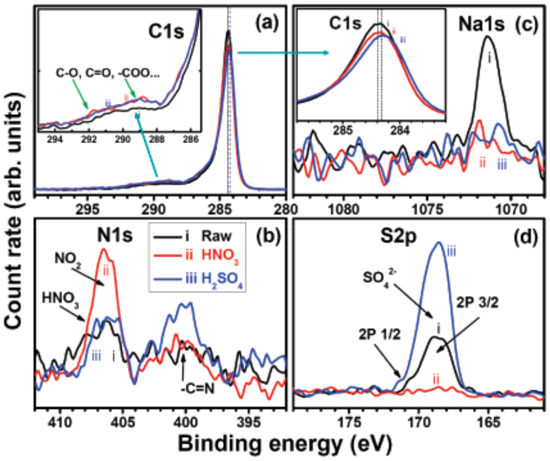

Figure 2. XPS spectra of (a) C1s, (b) N1s, (c) Na1s, and (d) S2p core levels from SWCNT thin films recorded before (i, black) and after 1 h HNO_3 (ii, red), and H_2SO_4 (iii, blue) acid treatment.

report that the chemical doping of the bucky paper (no SDS) by the oxidizing agent enhanced the conductivity significantly.[2,8,10]

Figure 3 presents Raman spectra with two excitation energies. At an excitation energy of 514 nm, the semiconducting nanotubes were excited as confirmed from the radial breathing mode (RBM) and G-band (no Fano line). The intensity of the G′-band, which is an overtone of the D-band, did not change appreciably. No appreciable peak shift in the G-band and RBMs was observed, independent of the treatment time from 20 to 100 min. At an excitation energy of 633 nm, metallic tubes were excited. One thing to note was the development of the Fano line at the lower energy side of the G-band, which is an evidence of the enhancement of metallicity in the film.[9] The Fano line after acid treatment was not fully recovered to that of the pristine SWCNTs. The enhancement of the G′-band intensity was saturated at longer treatment time. Nevertheless, no obvious peak shift in the G-band and no development in the D-band were observed, independent of treatment time. Thus, the effect of acid treatment we observed from the SDS-dispersed SWCNT TCFs is mainly the removal of SDS and enhancement of metallicity in the film and little influence from the chemical-doping effect. It seemed that the metallic tubes were more sensitive to SDS and acid treatment.[11]

The effect of acid treatment of SDS-dispersed SWCNT-TCFs is different from that of bucky paper. It has been well-known that the SDS can be washed off easily by water in the vacuum-filtration method.[3b] Although the washing was done several times and thus no appreciable amount of SDS was visible in FESEM image, some remaining SDS significantly degraded the sheet conductance because of their highly insulating nature. HNO_3 can efficiently remove the residual SDS among CNTs. XPS data strongly implies that a considerable amount of SDS was removed by acid treatment such that the conductivity of the film was significantly improved. Nevertheless no significant doping effect was observed. Even longer acid treatment time up to 2 h did not show significant doping effect. Oxidation that induces charge transfer from CNT to adsorbates and subsequently invoke *p-type* doping effect did not occur in our case. The presence of SDS on the CNT surface thus prevented SWCNTs from being oxidized. Another interesting effect of acid treatment is the densified film density. In general, the formation of sparse networks is a serious drawback of the spray approach. The removal of SDS and subsequent densification of the film thickness was achieved by the simple acid treatment. The resistance of the film can be defined as a sum of CNT resistance and the cross-junction resistance. The enhancement of metallicity clearly reduced the resistance of SWCNTs themselves. The contact resistance was significantly improved by removal of SDS among cross-junctions. The densification of the film density improved the conductivity by ∼25%. These two contributions enhanced the conductivity of the film by a factor of ∼4 times. The film was stable in air for a long time (Figure S4), unlike the conducting polymer-doped film. This environmental chemical stability is another advantage of the CNT film. Our approach of CNT film preparation and chemical treatment is easy and straightforward for large-size and could open new opportunities in the development of next-generation flexible displays.

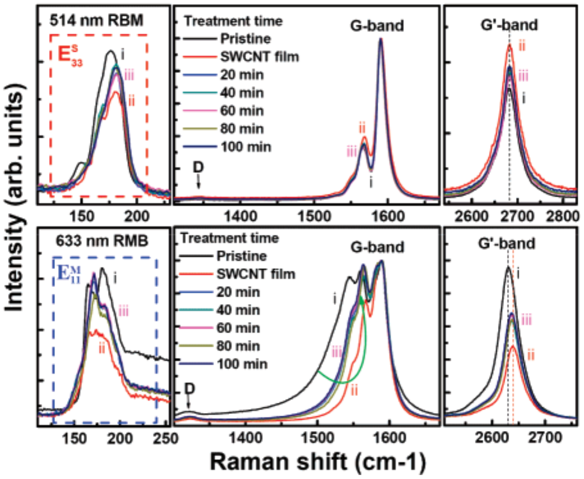

Figure 3. Raman spectra of SWCNT thin films at an excitation energy of 514 and 633 nm before (ii, red) and after different nitric acid treatment times of 20∼100 min (iii, colored) compared with pristine SWCNT powder (i, black). Peaks are normalized with respect to the G-band intensity.

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Note Added after ASAP Publication. Typographical errors were corrected on May 31, 2007.

Supporting Information Available: Experimental procedures; Figure S1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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