Supporting Materials

Chemically-treated Single-walled Carbon Nanotubes as Digitated Penetrating Electrodes in Organic Solar Cells

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S1. Synthesis of SWCNT-network by ACCVD and the transfer and patterning process

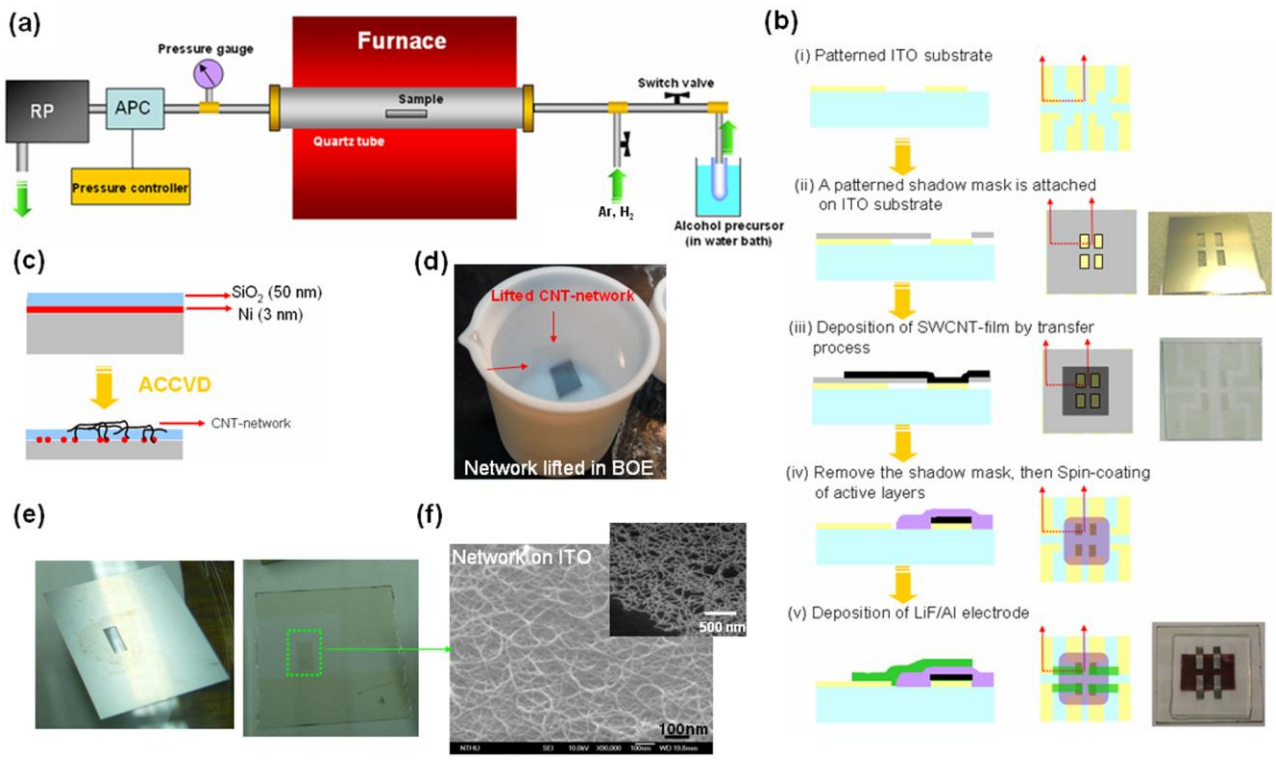
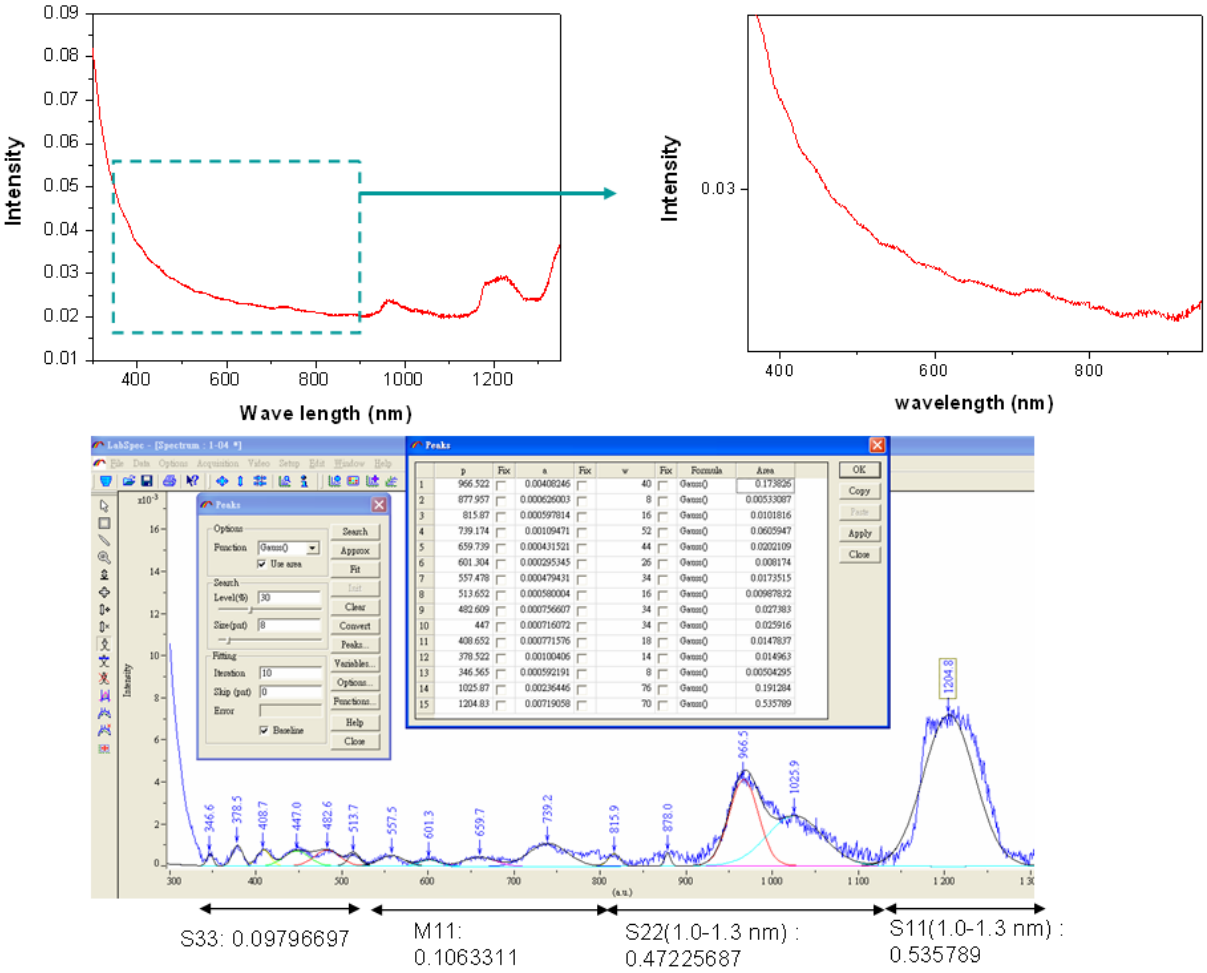


Figure S1. (a) The experimental setup of ACCVD system. (b) The process flow of device fabrication. (c) Illustration of substrate [Ni (3 nm)/porous SiO_2 (50nm) deposited by electron-beam evaporation in sequence on a silicon wafer with 300-nm thermal SiO_2] for the growth of SWCNT network and after growth by ACCVD (d) Photograph image show that SWCNT network floating on the solution surface after

BOE. (e) The process to define the pattern of SWCNT network on a pre-patterned ITO substrate with a shadow mask. (f) The SEM image of SWCNT network transferred on the substrate as indicated in (e). The inset in (f) shows high-contrast morphology observed by the so-called low-voltage SEM method (0.5 KV).

S2. Characterization of as-grown SWCNT network: s-SWCNTs/m-SWCNTs

Here, we employed optical absorbance spectra to quantitatively evaluate the ratio of (i.e., s-SWCNT:m-SWCNT) our as-grown SWCNT network. The baseline correction method is based on the work described by *Green et al.*[S1]. The as-grown SWCNT-network was first transferred onto a quartz substrate for this measurement. After the background signal of the acquired curve was subtracted, the fitted peaks were integrated to calculate the species ratio by the software of LabSpec. For statistical analysis of the ratio, six SWCNT networks were taken and evaluated. The result show that the percentage of s-SWCNTs in this film is 71.3~82.0%.

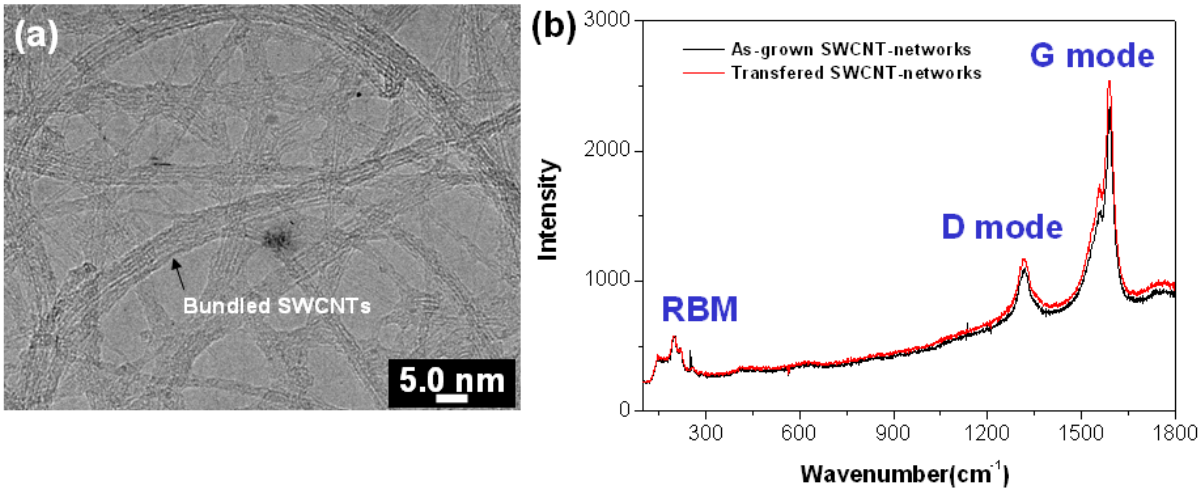


References

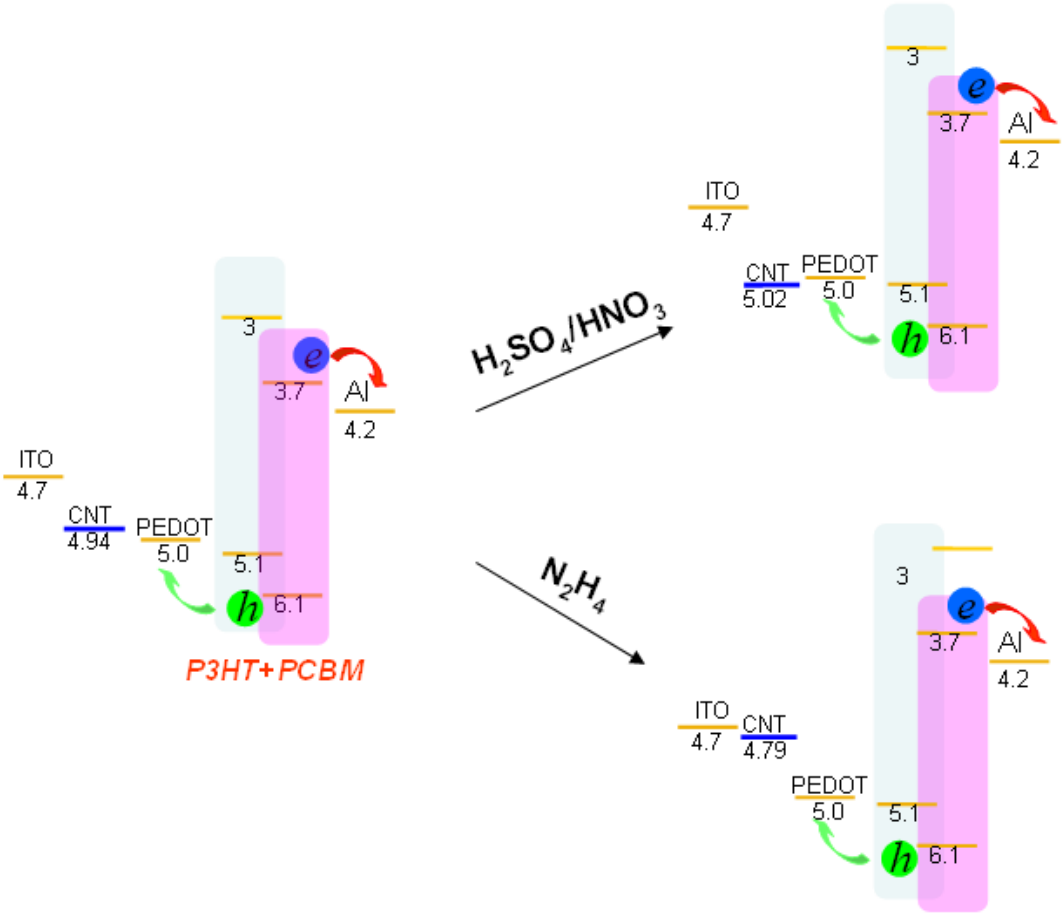
[S1] A. A. Green, M. C. Hersam, *Nano Letters* **2008**, 8, 1417.

S3. Characterization of SWCNT network before and after the transfer process: HRTEM and Raman spectra

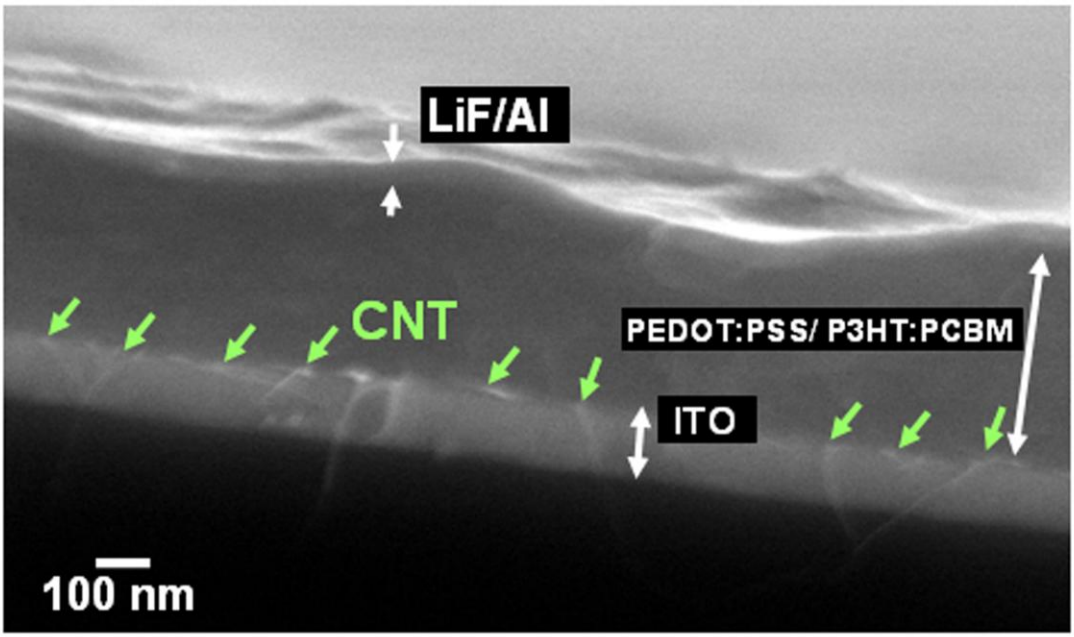
The CNT network is transferred to the copper grid and a glass substrate for the TEM and Raman characterization, respectively. From the TEM observation, there are no obvious impurities (such as residual SiO_2 clusters or metal particles) in SWCNT network. The Raman spectra as in (b) show comparable D/G ratio (i.e., 0.094 and 0.107 respectively) for the SWCNT network before and after the transfer process.

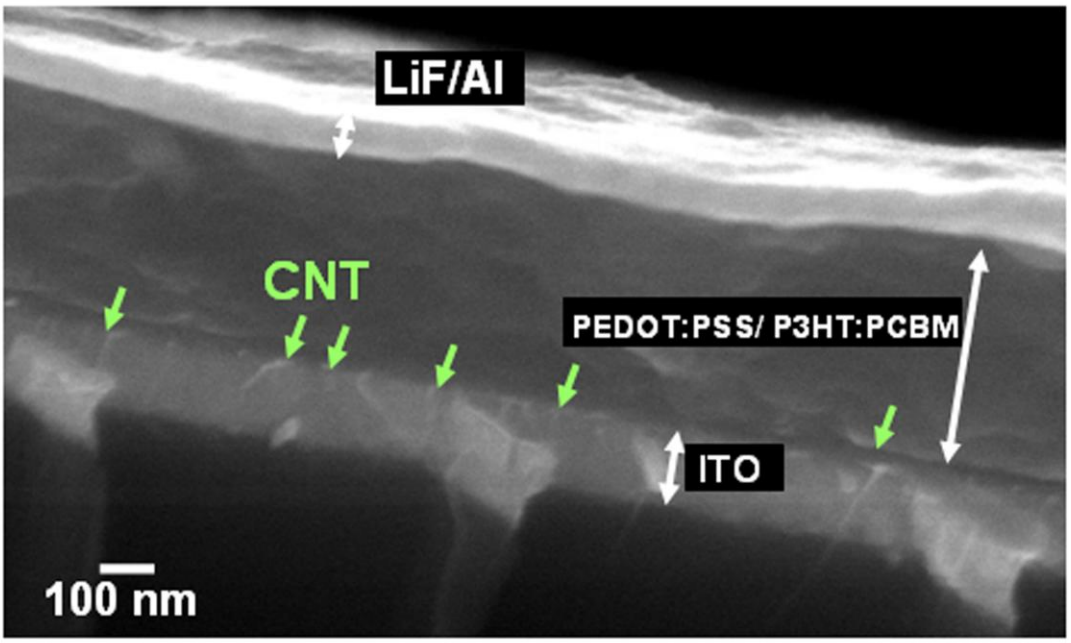


S4.The band diagrams showing the change in the work function of our SWCNTs subject to the H_2SO_4/HNO_3 or N_2H_4 treatment.

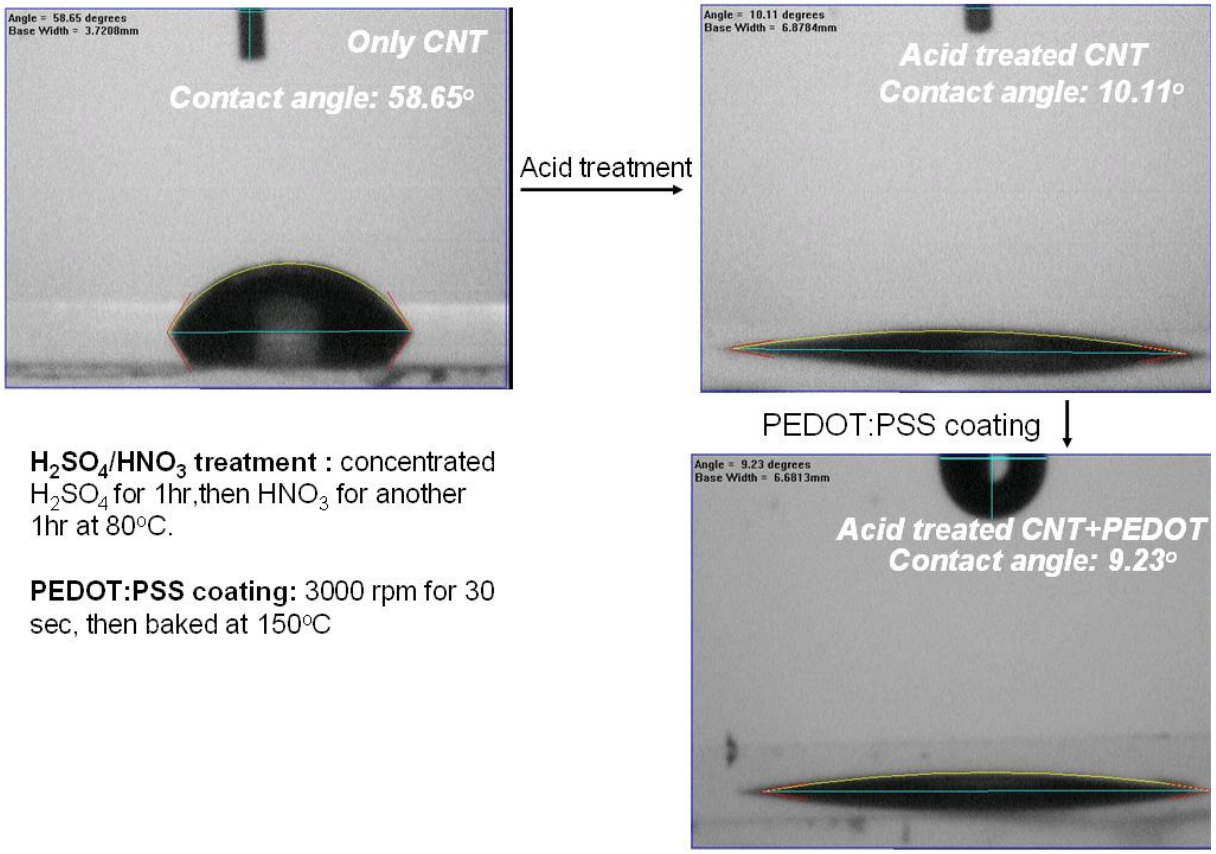


S5 Cross-section SEM on devices with H_2SO_4/HNO_3-treated SWCNT networks (original device structure: ITO/ SWCNT/PEDOT:PSS/P3HT:PCBM/LiF/Al)





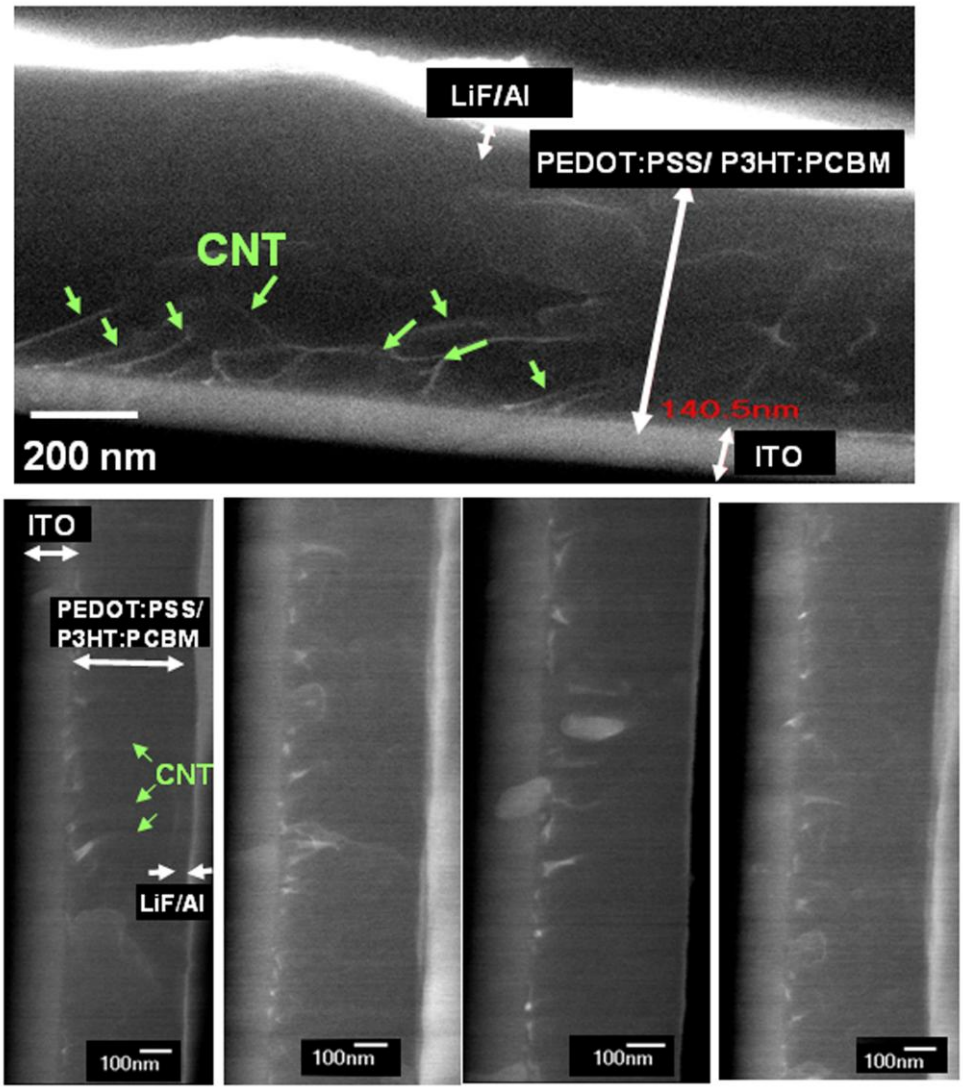
S6. The contact angle of H_2SO_4/HNO_3-treated SWCNT network



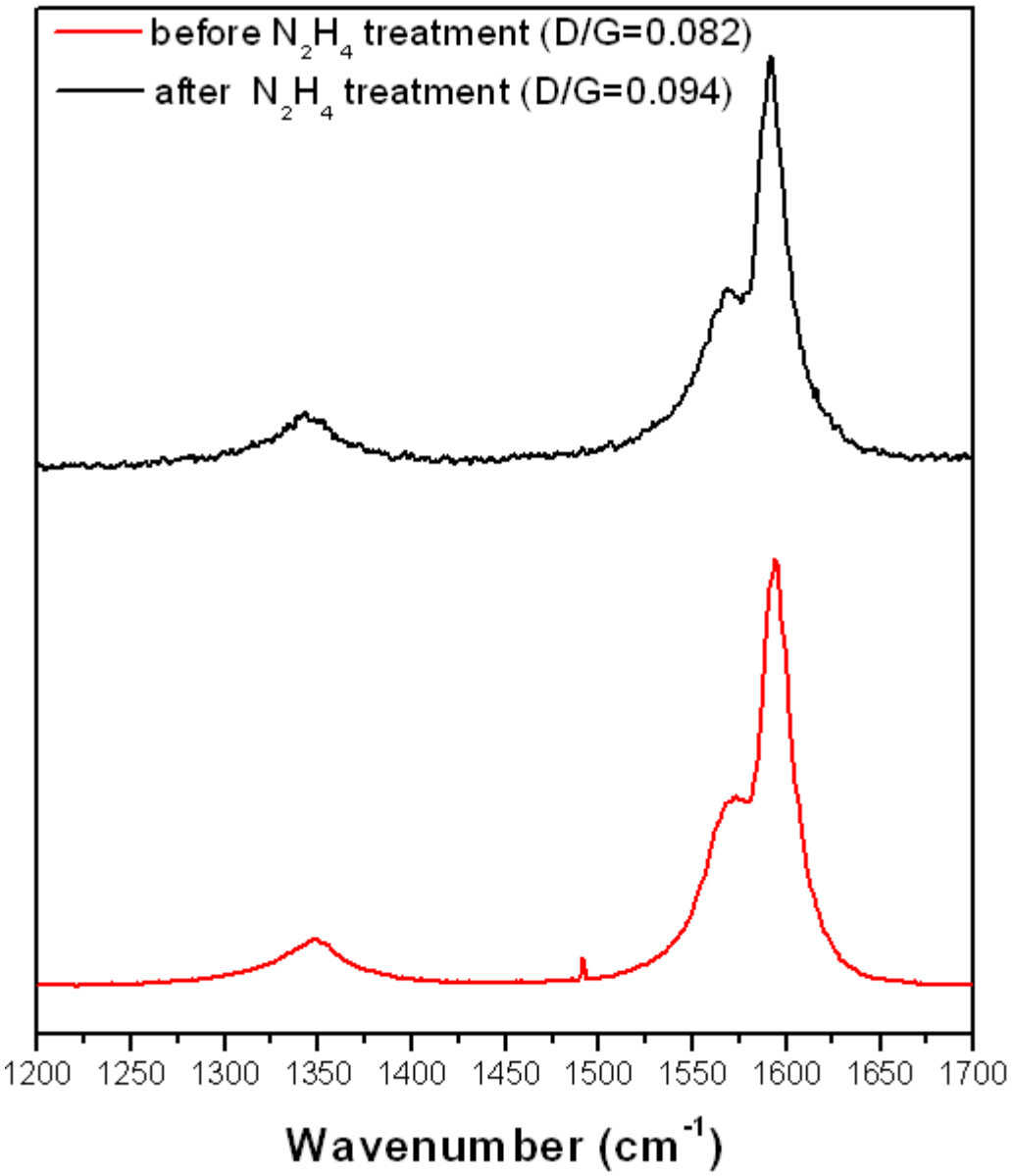
H_2SO_4/HNO_3 treatment : concentrated H_2SO_4 for 1hr,then HNO_3 for another 1hr at 80°C.

PEDOT:PSS coating: 3000 rpm for 30 sec, then baked at 150°C

S7 Cross-section SEM on devices with N_2H_4-treated SWCNT networks (original device structure: ITO/SWCNT/PEDOT:PSS/P3HT:PCBM/LiF/Al)



S8. The Raman spectra of SWCNT network before and after the N_2H_4 treatment



S9. The observed penetrating phenomenon imaged from more device cross-sectional analyses

The samples were cleaved for our SEM cross sectional analysis. We found that the artifacts tended to appear on poorly cleaved samples with relatively rugged cross sections (Figure S9-1a, a CNT-free reference device). When samples (also CNT-free reference devices) with nicely cleaved cross sections were examined, those cleaving-related artifacts were not observed (Figure S9-2).

In general, when examined under SEM, CNTs appear as bright streaks. In our study, we were particularly looking for CNTs imbedded (or partially imbedded) in polymer-based matrixes. When CNTs are imbedded in polymer matrixes, they appear as fussier and duller streaks (compared to exposed CNTs). As the image trace of a penetrating CNT could meander 3-dimensionally toward or away from the cross sectional plane in the polymer matrix, the brightness of the streak corresponding to a penetrating CNT can vary from segment to segment. A bright spot (or segment) can be observed when CNT is exposed on or out of the cross sectional plane.
After excluding SEMs with undesired artifact images, we basically followed the guidelines described above to identify the CNT showing penetrating phenomenon. For example, although Figure S9-1c is considered as an unsatisfactory SEM image for evaluating the CNT penetration phenomenon, some penetrating CNTs extending from the ITO substrate side are still discernible near the left bottom portion of the device cross section.

In addition to SEM images already presented in the paper, more images (with essentially no cleaving-related artifacts) obtained from additional devices are shown in Figures S9-3, S9-4 and S9-5..

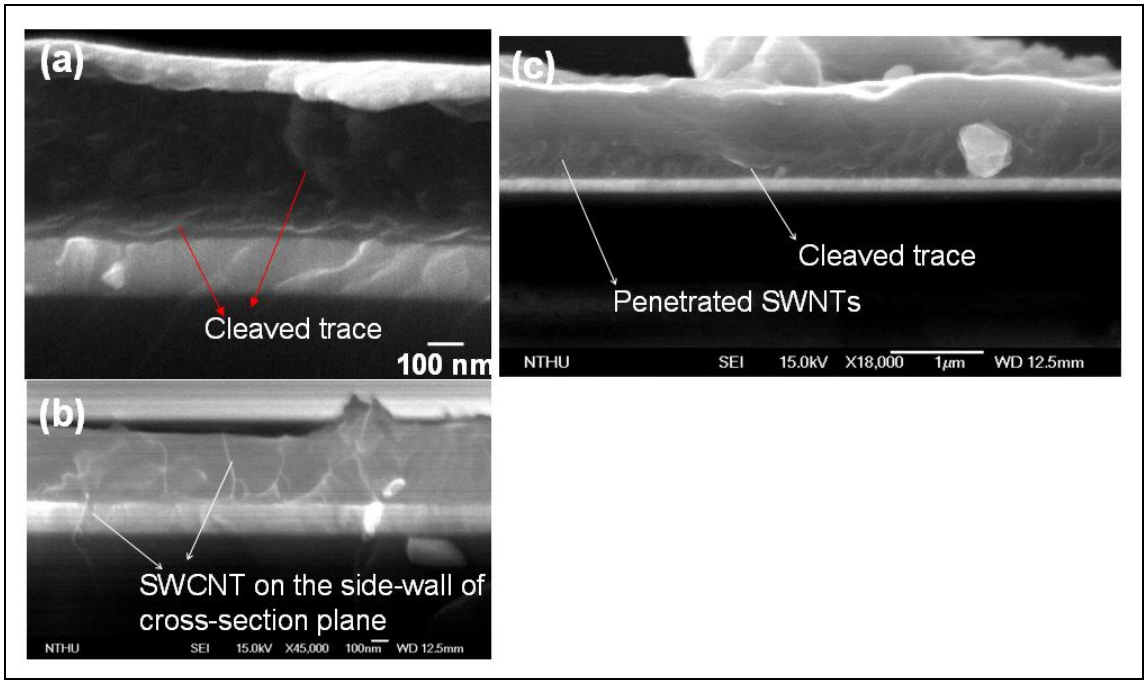


Figure S9-1. The cleaved trace observed in cross-sectional SEM.

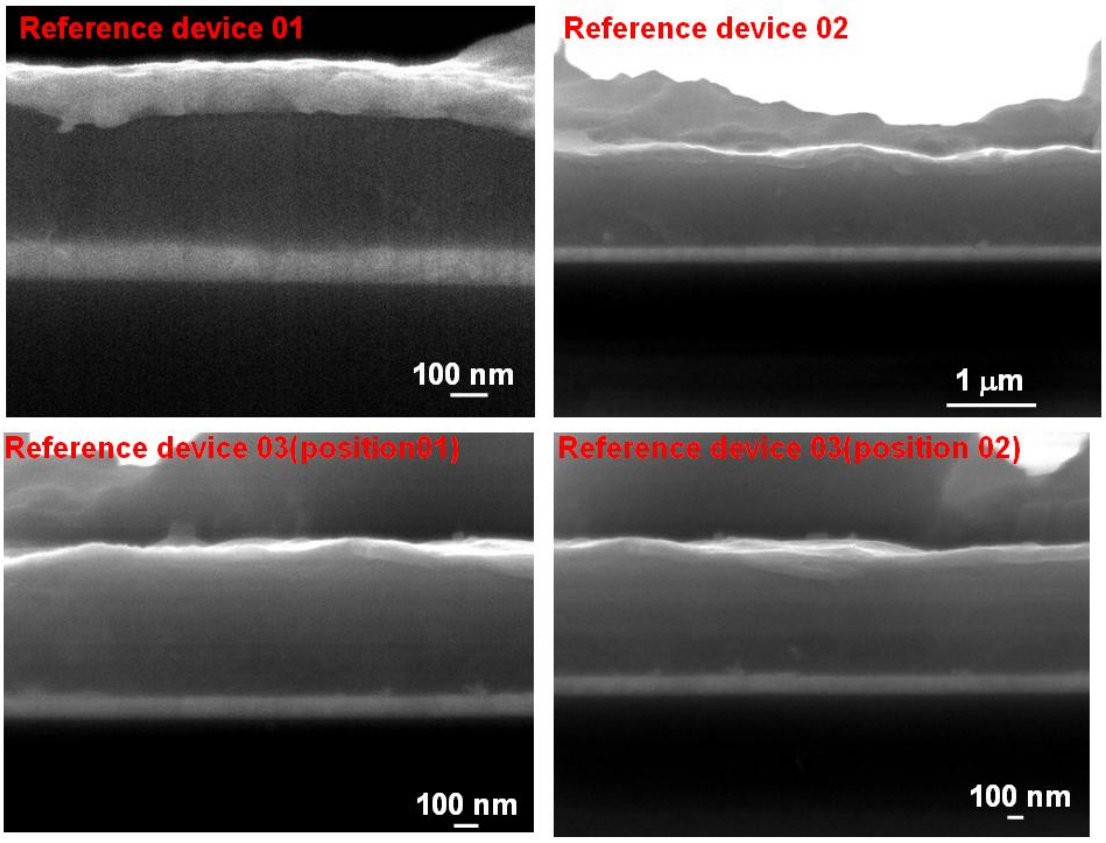


Figure S9-2. The cross-sectional images on reference devices (i.e., devices without introducing SWCNTs).

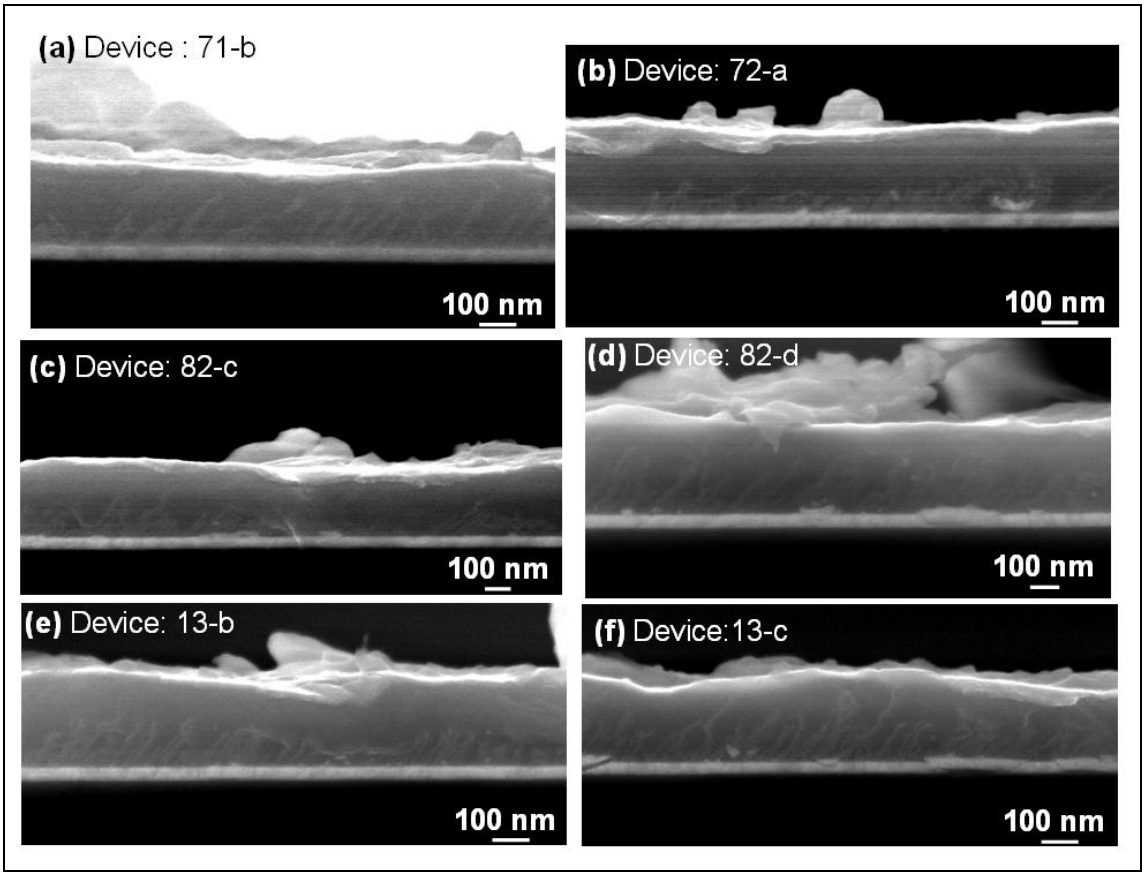


Figure S9-3. The penetrating phenomenon observed in different samples with introducing SWCNTs.

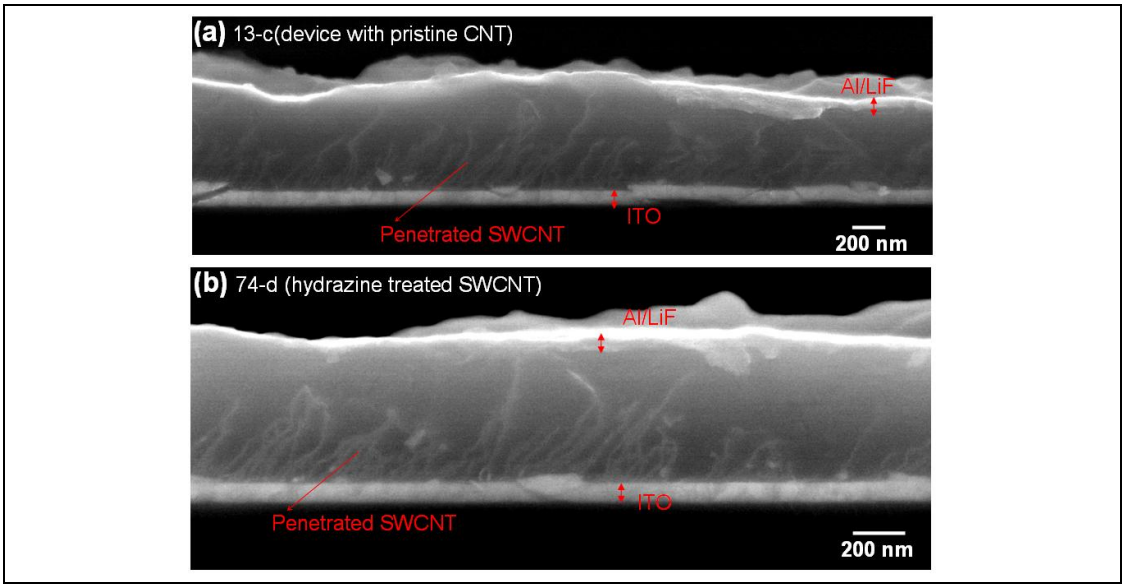


Figure S9-4. The penetrating phenomenon observed in (a) device with pristine SWCNT and (b) device with hydrazine-treated SWCNTs.

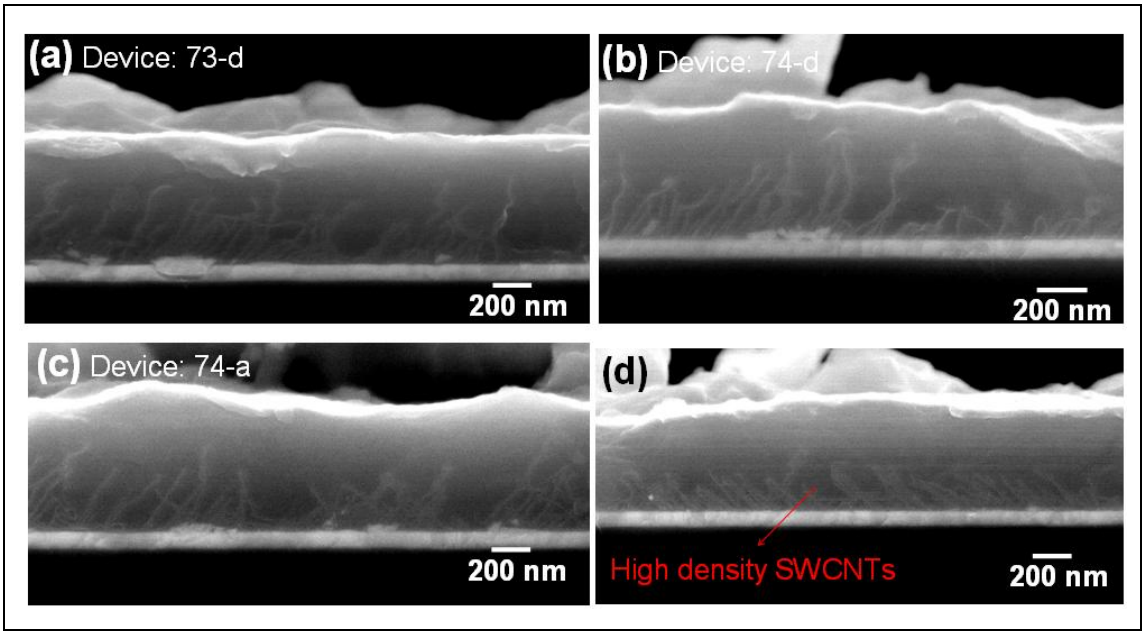


Figure S9-5. More cross-sectional SEM analysis on devices with hydrazine-treated SWCNTs.

S10 The contact angle of N_2H_4-treated SWCNT network