Supporting Information

Lithium Ions Intercalated into Pyrene-Functionalized Carbon Nanotubes and Their Mass Transport: A Chemical Route to Carbon Nanotube Schottky Diode

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Scanning photoelectron microscopy (SPEM)

The SPEM study was performed at the 8A1 (undulator U7) beam line at the Pohang Light Source (PLS). In SPEM, X-ray was focused by a diffractive X-ray lens (Fresnel zone plate), and the photoelectrons from the sample produced by the focused X-rays were analyzed by an electron energy anayzer. The focused X-ray size was 2 µm or better in horozontal direction (x axis) and ~0.5 µm in vertical direction (y axis).

Figure S1. UV-visible spectra of (a) pristine SWNTs, (b) 60 mM 1-pyrenemethylamine (1-PMA) solution in DMF, (c) 1-PMA functionalized SWNTs, (d) SWNTs after lithium intercalation.

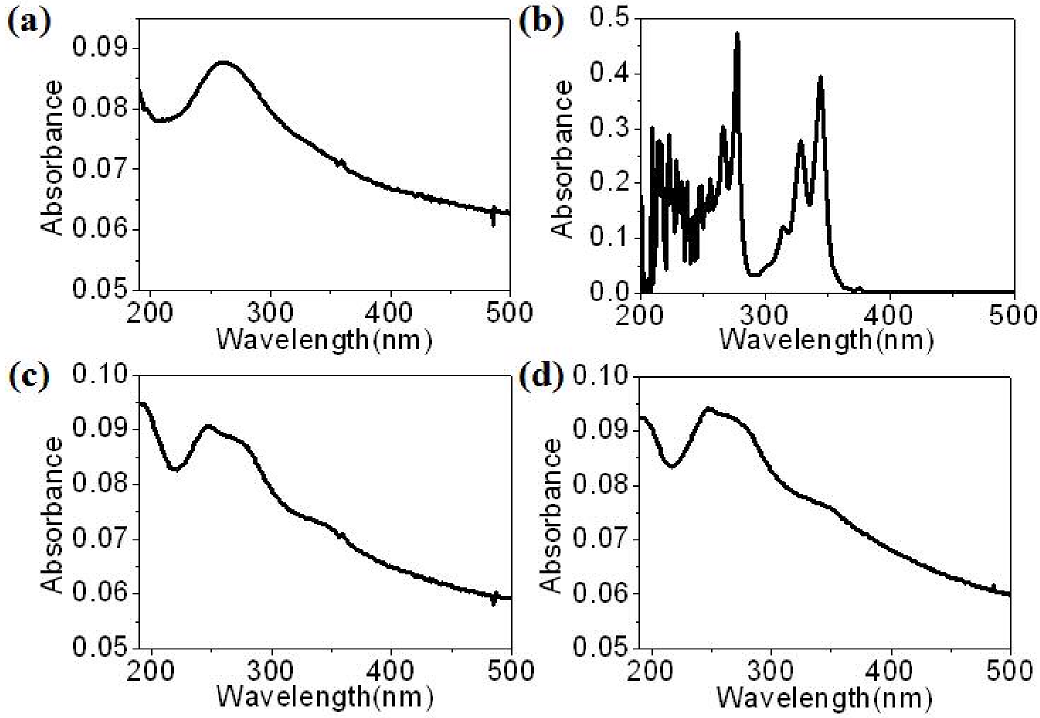


Figure S2. AFM images of non-intercalating metal nanoclusters formed on the 1-PMA functionalized SWNTs: (a) Cu^{2+}, (b) Ru^{2+}, (c) Sn^{4+} and (d) Zn^{2+}. SWNTs functionalized with 1-PMA were immersed into 100 mM of solutions of $CuCl_2$ (in ethanol), $RuCl_2$ (in ethanol), $SnCl_4$ (in methanol) and $ZnCl_2$ (in acetone), respectively.

Unlike lithium ion, transition metal ions are spontaneously reduced on the 1-PMA functionalized SWNT, hence topologically distinguishable corresponding nanoclusters are clearly observed. Note that the nanoparticle formation of transition metal on the 2,2':6',2"-terpyridine functionalized SWNT was previously reported.[1]

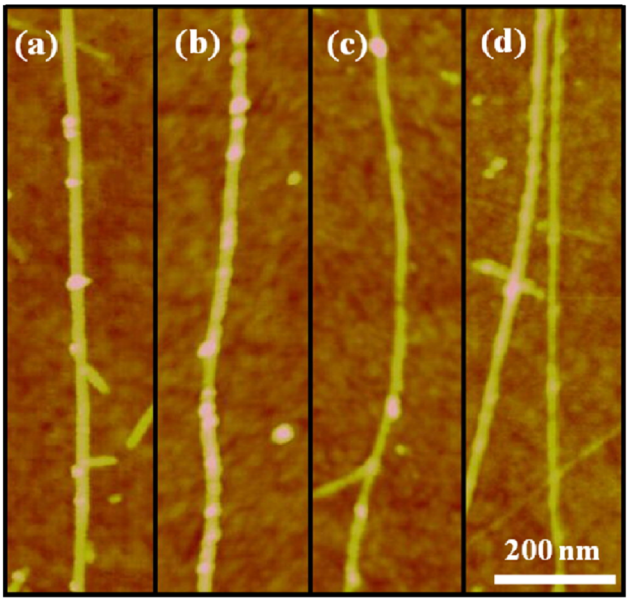


Figure S3. The enegy level chages upon the movement of lithium ions toward drain electrode. The work function of drain electrode is decreased (Δμ) by lithium ions transferred by electricfield, which induces large Schottky barrier (SB) between SWNT and drain electrode. The majority charge carriers (holes) in SWNTs can be transferred through the small SB by tunneling effect when positive bias voltage is applied to the drain electrode (left diagram). However, the hole transfer is not allowed when negative bias is applied to the drain electrode (right diagram) due to large SB. To decrease the SB, more negative gate voltage is necessary by which band energy is increased, so that the SB between SWNT and drain electrode is decreased and the hole tunneling can be possible. This explains the difference between V_{+TH} and V_{-TH}.

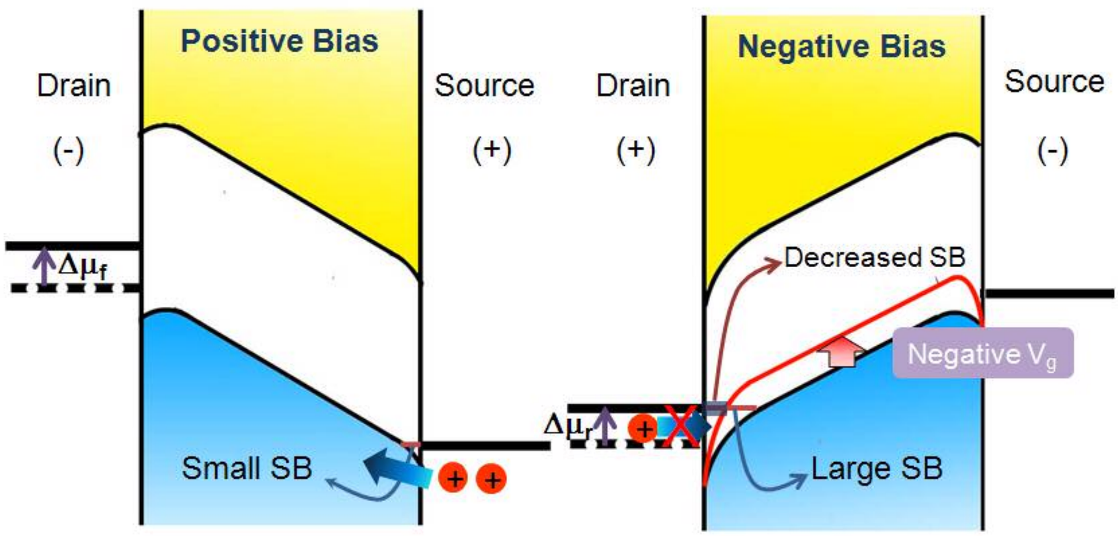


Figure S4. I-V_g curves of SWNT-FET devices. (black) pristine single tube SWNT-FET device, (red) after 1-PMA functionalization and (blue) after lithium treatment. The threshold voltage (V_{TH}) in the I-V_g curve was shifted to negative direction after 1-PMA adsorption, indicating electron donation from 1-PMA to SWNT. Although polycylclic aromatic compounds including 1-PMA are known to donate their π electrons to the conduction band of carbon nanotubes,[2] the V_{TH} shift by 1-PMA seems to be induced by the transfer of nonbonding electrons of amine group in 1-PMA because the V_{TH} shift is ignorable when 1-pyrenbutyric acid is adsorbed. The V_{TH} was then shifted back to positive direction, further than the original position, when lithium ions were intercalated (blue). This phenomenon owes to the electron transfer from SWNTs to lithium ions, leaving SWNTs with increased hole carrier density. It has been reported that lithium ions (Li^{+}) are reduced to about $Li^{+0.7}$ by electrons transferred from SWNTs when lithium ions are adsorbed on carbon nanotube walls.[3]

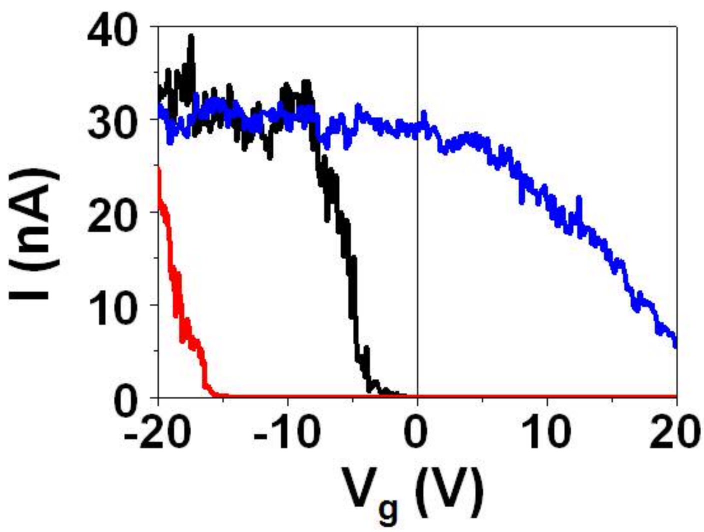


Figure S5. I-V curves ($V_g = 0$ V) upon the bias sweep from -5 V to +5 V(red), and from +5 V to -5 V (black).

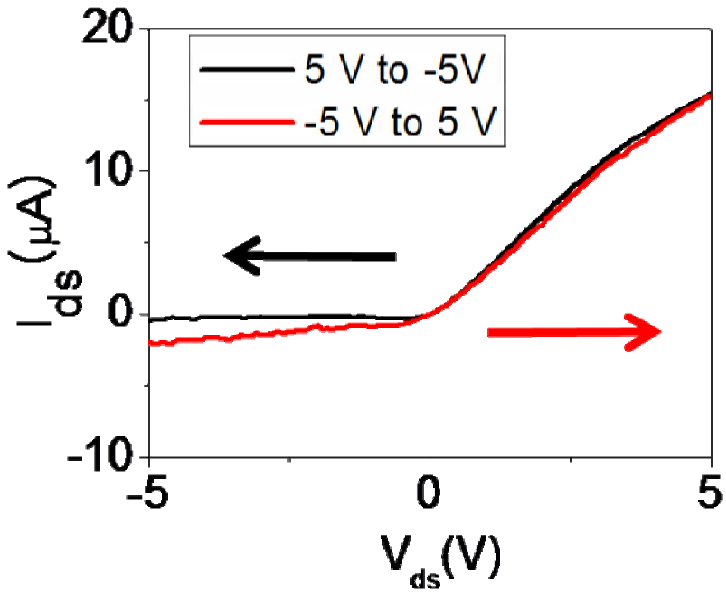
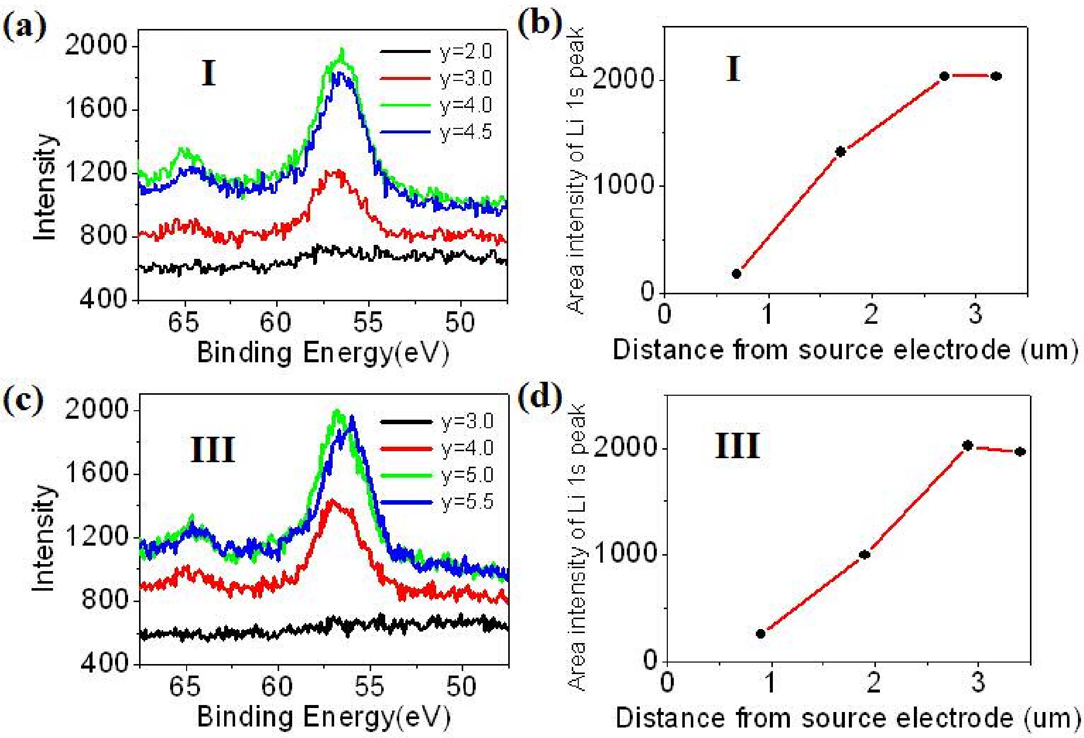


Figure S6. Space-resolved XPS Li 1s spectra obtained at different y positions at x positions of (a) I and (c) III in the Figure 3 in the main text. (b) and (d) are area intensities of the Li 1s peaks in (a) and (c), respectively.



References

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2. Lu, J.; Nagase, S.; Zhang, X.; Wang, D.; Ni, M.; Maeda, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Akasaka, T.; Gao, Z.; Yu, D.; Ye, H.; Mei, W. N.; Zhou, Y. *J. Am. Chem. Soc.* **2006**, *128,* 5115.

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