

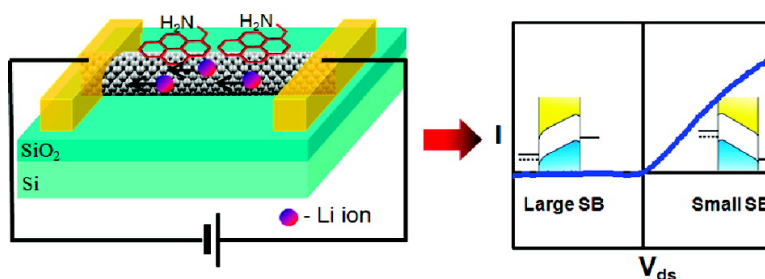
Communication

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

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Among the well-characterized various one-dimensional nanostructures, carbon nanotubes have been considered as a decent candidate for high-performance nanoelectronic device components due to their superb electrical properties.¹ A representative example is the single-walled carbon nanotube field effect transistor (SWNT-FET) device through which fundamental understanding of intrinsic electrical properties as well as successful demonstrations in sensitive chemical² and biochemical³ sensors has been realized.

Compared to the popularity of FET devices, carbon-nanotube-based diode devices have not been highlighted partially due to the complicated processes required for the fabrication. For example, complex fabrication steps involved with chemical doping are mandatory to accomplish both p- and n-type semiconducting carbon nanotubes in order to construct a p-n junction carbon nanotube diode.⁴ An alternative approach is to induce energetically asymmetric contact metal electrodes, from which carbon nanotube Schottky diodes are achievable due to the asymmetric work function energy levels.⁵ Although the Schottky diodes have advantages such as lower forward resistance and lower noise level than the p-n junction diodes, complex lithographic processes are still required to sequentially address two different types of metals for electrodes.

Herein, we report a simple chemical approach to modulate the work function of metal electrode via mass transport of lithium ions intercalated in the graphite-like pyrene-functionalized surface of carbon nanotubes.⁶ The transported lithium ions are supposed to be accumulated on the drain (−) electrode under the applied bias voltage and eventually demonstrate Schottky diode behaviors due to the provoked asymmetric work function energy levels (Figure 1a,b). Lithium ion is chosen because it has low work function and intercalates well to graphitic layers⁷ or multi-walled carbon nanotubes.⁸

Single channel SWNT-FET devices were fabricated as described earlier.⁹ In brief, SWNTs were synthesized at low yield directly on SiO₂/Si (300 nm thick SiO₂ layer on a highly doped p-type Si(100)) substrates by chemical vapor deposition (CVD) method, followed by addressing Cr (5 nm)/Au (20 nm) electrodes by using a conventional photolithography process. For the intercalation of lithium ions, the graphite-like layers were first formed on SWNTs via noncovalent functionalization of SWNTs with 1-pyrenemethylamine (1-PMA)¹⁰ by incubating the devices in 6 mM of 1-PMA dissolved in dimethylformamide (DMF) for 30 min at room temperature, followed by a thorough rinsing with DMF and isopropyl alcohol. The devices were then immersed in a lithium hexafluorophosphate solution (0.1 M LiPF₆ in a 1:1 mixture of propylene carbonate (PC) and dimethoxyethane (DME)) for 3 h. Note that this solution is popularly used for lithium ion battery.¹¹

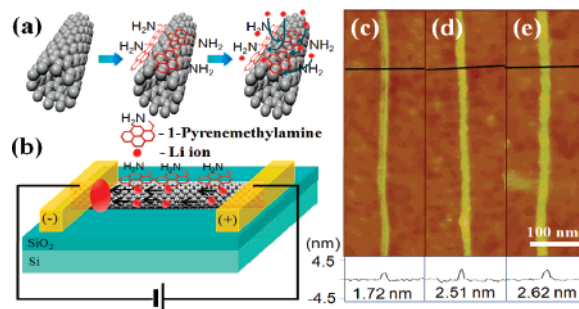


Figure 1. Schematic views of (a) noncovalent adsorption of 1-PMA on a SWNT and lithium ion intercalation, and (b) mass transport of lithium ions upon the application of bias voltage. AFM images of (c) a pristine SWNT, (d) after 1-PMA adsorption, and (e) after lithium ion treatment.

The devices were finally rinsed with 1:1 mixture of PC and DME, isopropyl alcohol, then dried under N₂.

The successful functionalization of 1-PMA on SWNTs was confirmed by UV-vis spectroscopy (Figure S1 in Supporting Information). As shown in Figure 1c,d, the coating of 1-PMA occurs very smoothly as no noticeable topological difference is observed, while the diameter of the SWNT is increased from 1.72 to 2.51 nm after 1-PMA treatment. Note that the AFM images were taken at the same position before and after the treatments. After lithium ion treatment, the surface still remains smooth while the height is slightly increased to 2.62 nm. This implies that lithium ions are believed to be intercalated between the 1-PMA and SWNT, instead of being clusterized via electrostatic interactions between amine functional groups in 1-PMA and lithium ions. If the latter occurs, topographically identifiable nanoparticles would have been formed on the sidewall of SWNTs, which is quite generic for other transition metal ion cases (Figure S2 in Supporting Information).

The electrical transport property changes were observed from $I-V$ and $I-V_g$ curves. The $I-V$ curves of SWNT-FET devices measured before and after 1-PMA adsorption (black and red lines in Figure 2a) show linear behaviors. However, the device shows clear diode-like $I-V$ curves when lithium ions are intercalated (blue curve in Figure 2a). As we postulated, this diode-like $I-V$ curve can be explained by the modulation of Schottky barrier between SWNT and metal electrodes: when the bias voltage is applied, lithium ions migrate toward the drain (−) electrode by the electric field. Lithium ions are then reduced at the SWNT–drain electrode junction, which causes the decrease in the work function of drain electrode, eventually increasing the Schottky barrier at the SWNT–drain electrode junction. Meanwhile, the SWNT–source electrode junction energy level remains unchanged (the energy level diagrams are shown in Figure S3). As a result, there is no current flow in the negative bias voltage range since the hole transport from drain electrode to SWNT is blocked. Such an asymmetric Schottky barrier

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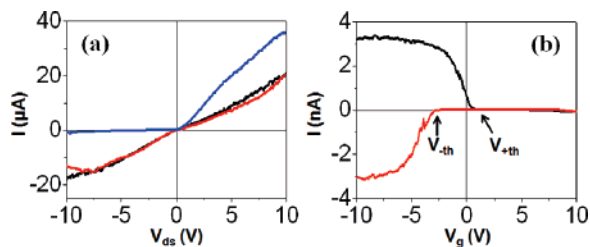


Figure 2. (a) I - V curves ($V_g = 0$ V), (black) pristine single tube transistor, (red) after pyrene adsorption, and (blue) after lithium treatment. (b) I - V_g curves of the single tube transistor after mass transport of lithium ions, (black) forward direction ($V_{ds} = 100$ mV) and (red) reverse direction ($V_{ds} = -100$ mV).

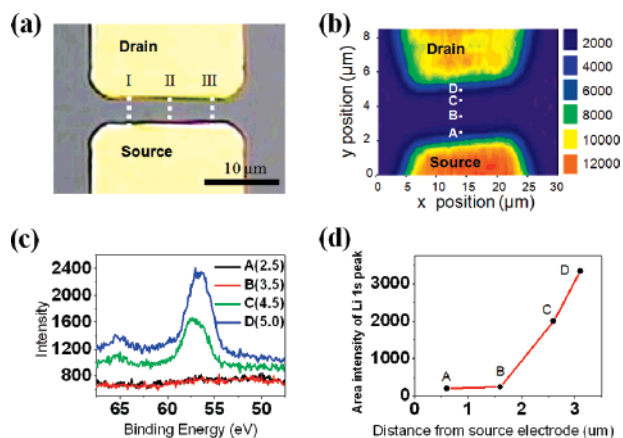


Figure 3. (a) An optical microscopy image of electrodes of the multi-tube transistor. (b) Intensity distribution of scanning photoelectron microscopy (SPEM) Au 4f image for the multi-tube transistor. (c) Space-resolved XPS Li 1s spectra obtained between the electrodes for the multi-tube transistor after lithium transport. A, B, C, and D are the positions marked in the image (b). (d) The area intensity of the Li 1s peak showing that the Li amount increased near the drain electrode.

is also evidenced by the different threshold gate voltages under the positive bias (V_{+TH}) and the negative bias (V_{-TH}) voltage applications (Figure 2b). In the gate voltage region between V_{-TH} and V_{+TH} , the drain current is in the ON state at the positive bias but in the OFF state at the negative bias.¹²

We also found that the diode-like devices did not exhibit hysteresis during I - V sweepings (Figure S5). This finding suggests that the movement of lithium ions is irreversible. More importantly, the graphite-like environment allowing intercalated lithium ions to be mobile is critical for this phenomenon since no such diode-like behavior is observed from the devices that are prepared without 1-PMA.

In order to confirm the mass transport of lithium ions, the population distribution of lithium was examined from diode-like devices by using scanning photoelectron microscopy (SPEM)¹³ and space-resolved X-ray photoelectron spectroscopy (micro-XPS). Due to the spectroscopic resolution limit, network-type SWNT-FET devices containing multiple numbers of SWNTs were used instead of single channel devices for the SPEM and micro-XPS studies.¹⁴ Figure 3a shows an optical microscope image of a network FET device having a ~ 3.5 μm gap between the source and drain electrodes. In order to define the spatial geometry of the device, we first obtained a SPEM image of the electrodes using the Au 4f photoelectrons (84 eV). Then, micro-XPS spectra were obtained

at different positions, 2.5, 3.5, 4.5, and 5.0 μm along the y -axis, as marked in the Figure 3b. The spatial resolution of the SPEM is 0.5 and 2 μm along the y - and x -axis, respectively. Figure 3c shows XPS spectra of Li 1s peaks obtained from each position (A–D). As expected, the area intensities of the Li 1s peaks are negligible at A and B positions close to the source electrode, while the highest intensity is found at the closest position (D) to the drain electrode (Figure 3d). The same population distributions were observed from different regions (I and III, also Figure S6 in Supporting Information). Hence, the SPEM results clearly support the idea that lithium ions are moved to the drain electrode by the applied bias voltage.

In summary, we demonstrated a facile chemical pathway for the realization of carbon nanotube Schottky diode devices. When a bias voltage is applied to lithium ions intercalated between the 1-PMA layer and the carbon nanotube surface, a mass transport of lithium ions occurs toward the drain (–) electrode. Such a mass transport of lithium ions successfully modulated the work function of contact electrode metals, resulting in the induction of asymmetric energy levels at both SWNT–source and SWNT–drain electrodes. The present approach using the concept of mass transport of lithium ions to modulate the metal contact characteristics is a simple but potent process that can be further applied to various nanomaterial-based electronic devices.

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Supporting Information Available: UV–vis spectra, experimental details of SPEM-XPS, and more data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The I - V_g curves of original SWNT-FET, after treatments with 1-PMA and lithium ions, are shown in Figure S4 in Supporting Information.
- (13) SPEM study was carried out at the 8A1 beamline of the synchrotron facility at POSTECH (Pohang Accelerator Laboratory, PAL).
- (14) Even with the network-type SWNT-FET devices, the Li 1s core-level peak could be detected with a reasonable S/N ratio after long spectral acquisition time for several minutes.

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