METAL-SEMICONDUCTOR TRANSITION OF ssDNA DECORATED SINGLE-WALLED CARBON NANOTUBES

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ABSTRACT
Here we experimentally verify the reversible change in electrical properties of single-walled carbon nanotube (SWNT) induced by a hybrid formation with ssDNA through π-stackin of nucleotide bases. The electrical response of the ssDNA-SWNT hybrid showed that the presence of water was crucial for causing metal-semiconductor transition. This transition was reversible when the hydration and dehydration was repeated and was not concerned DNA sequences. The results of Raman spectroscopy provide further evidence of metal-semiconductor transition of ssDNA-SWNT hybrids by water. We believe that ssDNA-(metallic) SWNT hybrids undergo the transition to the semiconducting property because the electrons of the metallic SWNTs lean toward to the ssDNA.

KEYWORDS: Single-walled carbon nanotube (SWNT), ssDNA-SWNT hybrid, metal-semiconductor transition

INTRODUCTION
The ssDNA forms a stable complex with an individual SWNT by the aromatic interactions between nucleotide bases and SWNT sidewalls, resulting in a wrapping configuration [1]. Recently DNA-SWNT hybrids have been spotlighted as intriguing bio-nano materials. The change of electrical property is one of the exciting phenomena resulting from the ssDNA-SWNT hybrid formation. This transition has been observed with indirect approaches such as Raman spectroscopy and UV/vis/NIR [2,3]. However, direct measurement of conductivity shift was rare and inconclusive [4]. Furthermore the detailed investigation of the change of electrical property by hybrid formation remains unexplored.

Here we report the first direct measurement of metal to semiconductor transition of SWNT through hybrid formation with ssDNA by helical wrapping. The unique electronic properties of the ssDNA-SWNT can be crucial to the development of next-generation nano-bio technique platforms. Therefore, a complete understanding of the ssDNA-SWNT binding mechanism and resulting electrical property change is essential for its applications.

EXPERIMENTAL
1. Preparation of ssDNA-SWNT hybrid
Metallic-dominant SWNTs (Carbon Nanotechnologies Inc. TX USA) made through the HiPCO process were sonicated in a 10 μM oligo DNA solution for 90 minutes. The resultant suspension was centrifuged at 15000 rpm for 60 min to remove large impurities in the sample. The sonication and centrifugation process were...
repeated twice. Surfactant-based dispersed SWNTs suspension was prepared by sonication and centrifugation process in 1% sodium dodecyl sulfate (SDS) solution for the reference.

RESULTS AND DISCUSSION

The electrical response of the sample was measured as shown in Figure 1. ssDNA-SWNT hybrids were assembled by dielectrophoresis (DEP) across pairs of electrodes. The DEP condition of 3 V @ 5 MHz resulted in the enrichment of metallic SWNT (Figure 2) [5]. 300 nm gap size of electrodes was used to remove CNT-to-CNT contact and only to see the interaction in the hybrid.

![Figure 1. Schematic of measurement setup](image1)

![Figure 2. ssDNA-SWNT hybrids were deposited on 300 nm gap size electrode with DEP. (a) SEM image. (b) Importance of gap width of the electrode](image2)

The surfactant-based dispersed pristine SWNT showed the metallic behavior regardless of the presence of water as expected in Figure 3(a). Figure 3(b) shows that water molecule is crucial for causing the change of electrical property due to hybrid conformation. In the dry state, $I_{SD}$ of hybrid was not significantly affected by the gate voltage. The identical sample after introducing D.I. water, however, clearly showed the behavior of p-type semiconductor. Furthermore this metal-semiconductor transition is reversible when the hydration and dehydration were repeated.

![Figure 3. Electrical characteristics of ssDNA-SWNT hybrid (a) Pristine SWNTs (b) ssDNA-SWNT hybrid, (poly C (dC) and poly G 18-mer was used)](image3)

![Figure 4. the results of repeatability test; (1) Initial dried sample, (2) First hydration, (3) First dehydration, (4) Second hydration, (5) Second dehydration (used sequence: 5'-aaa gga cga cat tag acg aa-3')](image4)
The results of Raman spectroscopy in Figure 5 provided another evidence of metal-semiconductor transition of ssDNA-SWNT hybrids by water. The G-modes of both pristine SWNT and hybrid in dry state have similar broad and asymmetric Breit-Wigner-Fano (BWF) line shape, which indicates metallic SWNT. After the injection of water into the dry sample, however, BWF line shape was almost diminished and shifted to high frequency. These results strongly suggest that the transition of the hybrid occurs only in water [5].

![Raman spectra](image)

We believe that the electrical change of ssDNA-SWNT hybrid originates from the charge transfer between the SWNT and ssDNA. This change did not happen in dry state because ssDNAs are electrically neutral. In contrast, ssDNAs are changed to negatively-charged ones after the hydration by water molecules. As a result, PO₄⁻ group of ssDNA becomes closer to the SWNT surface and the charge transfer between them occurs. The electronical interaction opens the energy band gap of the SWNT. This theoretical analysis agrees that the metallic SWNT wrapped by ssDNAs becomes a p-type semiconductor by water molecule.

CONCLUSIONS

We studied the electrical characteristic of ssDNA-metallic SWNT hybrid. The hybrid showed metallic behavior in dry state while p-type semiconducting behavior in wet state. We confirmed this phenomenon using FET measurement and Raman spectroscopy. We believe that it is caused by the charge transfer between the SWNT and ssDNA in water.

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REFERENCES