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Formation of quantum dots in single stranded DNA-wrapped single-walled carbon nanotubes

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The transport properties of single-stranded DNA (ssDNA) wrapped single-walled carbon nanotubes (SWNTs) are studied from low to room temperature. Atomic force microscopy reveals a regularly patterned geometry of ssDNA molecules on the surface of SWNTs. Our measurements indicate that the semiconducting behavior of SWNTs is drastically changed after ssDNA modification, showing a clear charge-transfer process at room temperature. At low temperatures single-electron tunneling features are observed up to 80 K, demonstrating clearly that quantum dots in series are created in the SWNTs due to the ssDNA wrapping. © *2010 American Institute of Physics*. [doi:10.1063/1.3284511]

The unique electrical properties of single-walled carbon nanotubes (SWNTs) make them good candidates for the building block of future nanoelectronic devices. In particular, the SWNT structure is considered to be suitable for forming channels of nanodevices based on quantum dots,[1–5] which can be used for single- or multiple-electron memory. During the past decade, many efforts have been devoted to fabricate single-electron transistors (SETs) by SWNTs. Normally, one SWNT channel serves as a single quantum dot in the configuration of field-effect transistors (FETs) if the SWNT has no defects, and a coulomb blockade effect can be clearly observed in SWNT-FET devices at low temperatures. Although a room temperature single-electron transistor has been reported by mechanically bending the SWNT by an atomic force microscope,[4,6] the dot size is hard to control. In addition, by introducing some defects into the surface of SWNTs or filling foreign materials into their inner space small size quantum dots are able to be created, and the devices often show the single-electron tunneling transport behavior.[7–9] However, during the above modification process, a damage effect in the structure of SWNTs is also inevitably incorporated, which may bring the disturbance into the size of formed quantum dots in SWNTs. Therefore, it is difficult to reproduce the same electrical transport property. On the other hand, DNA is one of the most promising molecules with unique properties and being proposed to be very potential candidates for nanoelectronics devices. Recently, the hybrid of single-stranded DNA (ssDNA) and SWNTs has been widely used to improve performance of FET devices and to construct chemical sensors.[10,11] Moreover, wrapping SWNTs with ssDNA molecules (ssDNA/SWNTs) can form regular surface patterns along the SWNTs, and the electronic structure is predicated to be influenced by the wrapped ssDNA molecules,[12–16] making them possible as natural candidates for SET construction. However, little attention has been paid to this important issue.

In this letter, we report the results of transport properties of ssDNA/SWNTs at low temperatures, showing clearly a single-electron tunneling feature, as reflected in the observation of coulomb oscillation peaks at low temperatures up to 80 K. Our results indicate that it is possible to create quantum dots by ssDNA wrapping. Furthermore, it is found that the length of wrapped ssDNA exhibits little effect on the size of formed quantum dots.

SWNTs used in this work were produced by an arc discharge using Fe/Ni as catalyst.[17] The synthesis of ssDNA/SWNTs was performed by applying a dc electric field in DNA solution, during which the ssDNA molecules are adsorbed onto the outside of SWNTs. The synthesis process of ssDNA/SWNTs is partially similar to the case of ssDNA encapsulated SWNTs using an Al substrate bias method in DNA electrolyte solution.[18] When a dc bias voltage ($V_{dc} = 10$ V) is applied to an Al anode electrode for 10 min, ssDNA molecules with negative charges are accelerated to the end-closed SWNTs deposited on the Al anode electrode.[19] It is known that DNA molecules exist with the random-coiled conformation in solution, and therefore, it is easy to decorate DNA molecules on the outside of SWNTs. The ssDNA/SWNT samples are examined in detail by atomic force microscopy (AFM) (JSPM-5400). After fabrication, ssDNA/SWNTs were extracted from the electrodes into solution of *N*, *N*-dimethylformamide (DMF) and spin-coated onto Au electrodes arranged in a FET configuration, and the FET device preparation has been described elsewhere in our previous letter.[20] The transport measurements are carried out in the temperature range of 10–300 K in vacuum on a semiconductor parameter analyzer (Agilent 4155C).

AFM images reveal a regular pattern of ssDNA on the surface of SWNTs, consisting of peaks and valleys in height along the length of each SWNT. Figure 1(a) shows an AFM image of SWNTs wrapped with 30 cytosine (C_{30}) ssDNA, and the bottom inset of Fig. 1(a) shows the height profile of C_{30} ssDNA/SWNTs, which enables us to identify the DNA molecules which are coiled to ball-like clusters on the nanotube surface. The nanotube height above a Si substrate is about 1.4 nm. The width of peaks along the nanotubes is 5–10 nm, and the average peak to peak distance is about 23 nm. For comparison to C_{30} ssDNA wrapped SWNTs, an AFM image of C_5 ssDNA/SWNTs and its corresponding height profile are shown in Fig. 1(b) and its bottom inset, respectively, where DNA molecules display a similar ball-like cluster morphology on the surface of SWNTs. This result suggests that the ssDNA with different lengths show almost no effect on the ssDNA/SWNT structure, which agrees with a previous report.[14]

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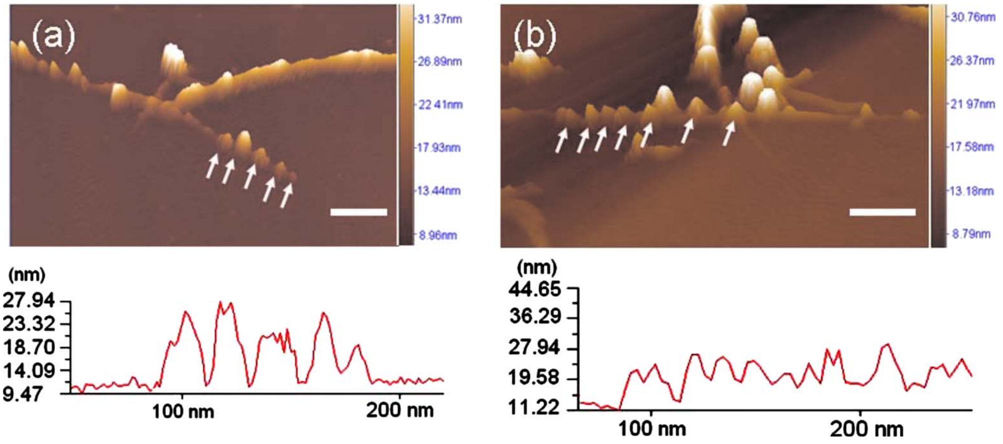

FIG. 1. (Color online) AFM images of SWNTs wrapped with C_{30} ssDNA (a) and C_5 ssDNA (b) (Scale bar: 50 nm). The bottom insets show height profiles along the corresponding parts of ssDNA/SWNTs (indicated by arrows).

The electrical transport properties of SWNTs are found to change significantly after wrapping by DNA molecules. The transfer characteristic of pristine SWNTs with source-drain current measured as a function of gate voltage (I_{DS}-V_G) under the FET configuration shows the known *p*-type behavior with a threshold voltage of less than −30 V, as described in Fig. 2(a). In contrast, the threshold voltage is shifted to about 0 V for *p*-type C_{30} ssDNA/SWNT, as seen in Fig. 2(b), and this demonstrates a charge transfer process. This finding implies evidently that the electronic structure of SWNTs is tuned by ssDNA molecules. More interestingly, with decreasing the temperature regular coulomb oscillation peaks are observed in the SWNT at 10 K, as seen in Fig. 2(c). In contrast, in our case such regular oscillation peaks have never been observed in pristine semiconducting SWNT-FET devices at low temperatures. The oscillation peaks in V_g are evenly spaced at $\Delta V_g = 1.9 - 2.1$ V, therefore, this result indicates that quantum dots in series are created in the SWNTs owing to ssDNA wrapping. By considering the low gate efficiency (less than 10%) originated from a thick oxide in our device construction,[20] the gate capacitance is estimated to be $C_g = e/\Delta V_g = 7.6 - 8.4 \times 10^{-19}$ F. The size of quantum dots is estimated to be in the range of 25–30 nm or larger according to our previous letters,[20,21] which is comparable to the ssDNA distribution on the SWNT and much smaller than the geometrical tube length, and the coulomb charging energy $E_c = e^2/2C_g$ is less than 95–110 meV. Figure 2(d) shows the I_{DS} measured as a function of source-drain voltage (V_{DS}) in the range of (−0.6)–0.6 V, where a series of well-pronounced current steps, namely, coulomb staircase behavior, is clearly identified in the I_{DS}-V_{DS} curve at $V_G = -20$ V. This can be explained by the incremental increase in the current at voltages where it is energetically favorable for an additional electron to sit on the quantum dot, which is well consistent with the observation in Fig. 2(c), revealing a clear signature of single-electron tunneling in the device. The average separation of the first and second current steps from Fig. 2(d) is about 200 meV, and therefore the discrete energy level spacing ΔE is determined to be $\Delta E = (200/2)$ meV $= 100$ meV, which is of the same order of the charging energy.

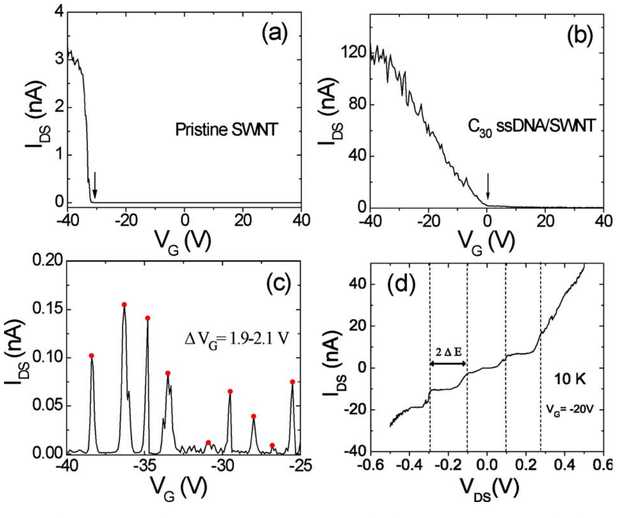

FIG. 2. (Color online) Source-drain current (I_{DS}) vs gate voltage (V_G) characteristics measured with bias voltage $V_{DS} = 0.1$ V at room temperature for (a) a *p*-type pristine SWNT and (b) a *p*-type C_{30} ssDNA/SWNT. (c) I_{DS}-V_G characteristic for a C_{30} ssDNA/SWNT FET measured with bias voltage $V_{DS} = 10$ mV at 10 K. (d) I_{DS}-V_{DS} characteristic measured with bias voltage $V_G = -20$ V at 10 K.

Figure 3(a) shows the gate-voltage dependence characteristics of the I_{DS} measured with V_{DS} ranging from −0.2 to 0.2 V. The *p*-type current shows clear oscillation peaks with a decrease in the absolute value of source-drain biases. The peak and valley positions of coulomb oscillations display an asymmetric feature at positive and negative V_{DS}. Some oscillation peaks have a high current, but other peaks have a low current. The multitude of peaks indicates that multiquantum dots are involved in the transport. Also, with respect to the I_{DS}-V_{DS} characteristics measured at 10 K, as represented in Fig. 3(b), we have further confirmed the single-electron tunneling transport behavior in C_{30} ssDNA/SWNT FET de-

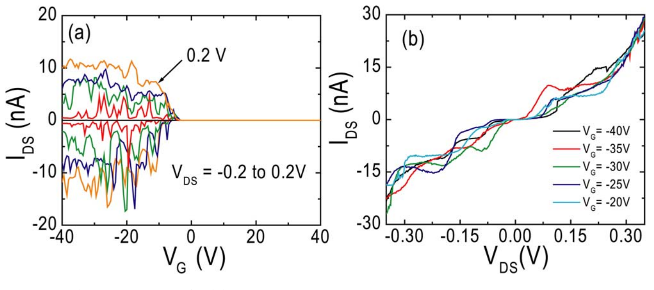

FIG. 3. (Color online) (a) I_{DS}-V_G characteristic for a C_{30} ssDNA/SWNT FET device measured with V_{DS} in the range of (−0.2)–0.2 V in steps of 0.04 V at 10 K. (b) I_{DS}-V_{DS} characteristics for a C_{30} ssDNA/SWNT measured with V_G ranging from −20 to −40 V in steps of 5 V at 10 K.

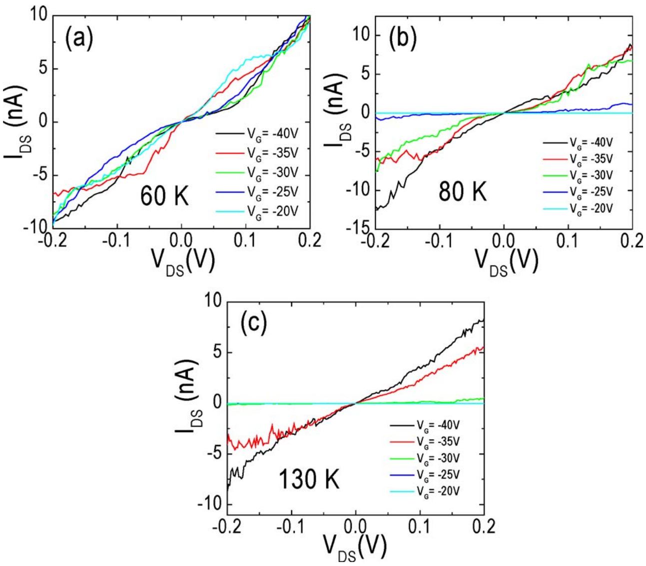

FIG. 4. (Color online) I_{DS}-V_{DS} characteristics for a C_{30} ssDNA/SWNT FET device measured with V_G ranging from −20 to −40 V at different temperatures: (a) 60, (b) 80, and (c) 130 K.

vice. When the gate voltage is changed from −20 to −40 V, the current step features shift along the source-drain bias axis, revealing evidently these current steps are associated with energy levels of quantum dots, somewhat in agreement with the observations in Fig. 3(a). Figure 4 depicts the temperature dependence of I_{DS}-V_{DS} characteristics measured at different gate voltages. With increasing temperature, the width of current step becomes much larger, as shown in Fig. 4(a), where the width of coulomb staircase measured at 60 K is 1.5 times larger compared with that observed in 10 K. In addition, on raising the temperature the source-drain current gradually indicate a strong gate-voltage dependence characteristic, as recognized in Figs. 4(b) and 4(c), and the staircase-shaped current disappears at 130 K. Furthermore, we have studied the ssDNA length dependence on the transport properties of SWNTs at low temperatures. In Fig. 5 the I_{DS}-V_G characteristics are measured at V_{DS}=20 mV from 10 to 130 K for a C_5 ssDNA/SWNT FET device. Surprisingly, oscillation peaks with ΔV_g of 1.3–1.9 V resulted from coulomb blockade are observed, similar to those observed for C_{30} ssDNA/SWNT, suggesting that quantum dots with similar size are fabricated in the C_5 ssDNA/SWNT. This finding implies that the size of quantum dots is independent of the length of wrapped ssDNA, which is somewhat in consistence with AFM characterizations (Fig. 1) in which both of them display the similar helical wrapping geometry. Additional evidence is that the coulomb blockade phenomenon observed in the C_5 ssDNA/SWNT becomes less pronounced when the temperature is increased from 10 to 130 K, therefore, the temperature limitation for observing coulomb blockade is quite similar to that of C_{30} ssDNA/SWNT.

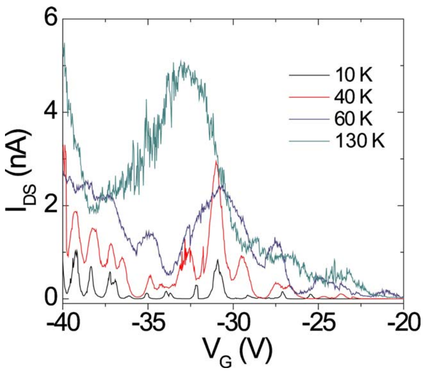

FIG. 5. (Color online) I_{DS}-V_G characteristics for a C_5 ssDNA/SWNT FET device measured with V_{DS}=20 mV at different temperatures.

In conclusion, the single-electron tunneling behavior is observed in ssDNA wrapped SWNTs at low temperatures. Compared with pristine SWNTs, periodic coulomb oscillation peaks are clearly observed up to 80 K in ssDNA/SWNTs, which opens the possibility of creating quantum dots in nanotubes by ssDNA decoration. It is found that the quantum dots formed in C_{30} and C_5 ssDNA wrapped SWNTs have the similar size distribution, which is possibly due to the fact that both of them have the similar ssDNA wrapping geometry. By more controlled ssDNA modification of SWNTs, such as well-defined ssDNA wrapping, our method can provide a prospective approach of creating quantum dots in SWNTs with high reproducibility and controllability.

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[1] S. J. Tans, R. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Georliga, and C. Dekker, Nature (London) **386**, 474 (1997).

[2] M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zell, A. Thess, and R. E. Smalley, Science **275**, 1922 (1997).

[3] S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).

[4] H. W. C. Postma, T. Teepen, Z. Zhao, M. Grifoni, and C. Dekker, Science **293**, 76 (2001).

[5] C. Dekker, Phys. Today **52**, 22 (1999).

[6] J. Y. Park, Y. Yaish, M. Brink, S. Rosenblatt, and P. L. McEuen, Appl. Phys. Lett. **80**, 4446 (2002).

[7] J. B. Cui, M. Burghard, and K. Kern, Nano Lett. **2**, 117 (2002).

[8] T. Kamimura, K. Yamamoto, and K. Matsumoto, Jpn. J. Appl. Phys., Part 1 **43**, 2771 (2004).

[9] J. Kong, C. Zhou, E. Yenilmez, and H. Dai, Appl. Phys. Lett. **77**, 3977 (2000).

[10] Y. Lu, S. Bangsaruntip, X. Wang, L. Zhang, Y. Nishi, and H. Dai, J. Am. Chem. Soc. **128**, 3518 (2006).

[11] M. T. Martínez, Y. C. Tseng, N. Ormategui, I. Loinaz, R. Eritja, and J. Bokor, Nano Lett. **9**, 530 (2009).

[12] M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, and D. J. Walls, Science **302**, 1545 (2003).

[13] M. S. Strano, M. Zheng, A. Jagota, G. B. Onoa, D. A. Heller, P. W. Barone, and M. L. Usrey, Nano Lett. **4**, 543 (2004).

[14] J. F. Campbell, I. Tessmer, H. H. Thorp, and D. A. Erie, J. Am. Chem. Soc. **130**, 10648 (2008).

[15] R. R. Johnson, A. T. C. Johnson, and M. Klein, Nano Lett. **8**, 69 (2008).

[16] D. A. Yarotski, S. V. Kilina, A. A. Talin, S. Tretiak, O. V. Prezhdo, A. V. Balatsky, and A. J. Taylor, Nano Lett. **9**, 12 (2009).

[17] K. Tohji, T. Goto, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga, and Y. Nishina, Nature (London) **383**, 679 (1996).

[18] T. Okada, T. Kaneko, R. Hatakeyama, and K. Tohji, Chem. Phys. Lett. **417**, 288 (2006).

[19] See supplementary material at http://dx.doi.org/10.1063/1.3284511 for supporting information.

[20] Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada, and T. Kato, Appl. Phys. Lett. **89**, 083117 (2006).

[21] Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada, and T. Kato, Appl. Phys. Lett. **89**, 093110 (2006).