

Single-Walled Carbon Nanotube Network based Biosensors using Aptamers and its Characteristics

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ABSTRACT

We have successfully demonstrated the single-walled carbon nanotube (SWNT) network based biosensor using aptamers as a protein recognition site. Aluminum was first patterned on the substrate with CVD-grown oxide. Then, gold was electrolessly plated on the Al electrodes and SWNTs were dip-coated on the substrate. Electrical pulses were applied through the electrodes to reduce a contact resistance. Finally, aptamers were attached on the surface of SWNTs and were used as a recognition site of human serum albumin (HSA). Carbon nanotube shows that it can be a powerful candidate for the next-generation sensor element for the biological/chemical detection.

Keywords: Single-walled carbon nanotube network, Biosensor, Aptamer, Human Serum Albumin

1 INTRODUCTION

Since its discovery in 1991 by Iijima, carbon nanotube (CNT) has attracted a lot of attention from researchers [1]. Much effort has been made to fabricate biosensors with carbon nanotubes as sensor elements due to their several advantages including large surface-to-volume ratio, one-dimensional electronic structure, and a molecular composition consisting of only surface atoms.

In this paper, we present a SWNT network based biosensor using aptamer and its experimental results. CNT network was used in the expectation that it will show a better performance and consistency in comparison with the single nanotube in that they contain a number of carbon nanotubes with various chirality and diameter making them have better uniformity in electrical properties [2]. Aptamers are artificial oligonucleotides (DNA or RNA) that can bind to a variety of materials with high selectivity, specificity. Since aptamers (1-2 nm) are much smaller than proteins, it is likely that aptamer-protein binding occurs inside the electrical double layer, which is characterized by Debye length (~3 nm in 10 mM ionic concentration), of solution resulting in higher sensitivity. The possibility to fabricate biosensors using SWNT network and aptamers is investigated.

2 DEVICE FABRICATION AND EXPERIMENTAL RESULTS

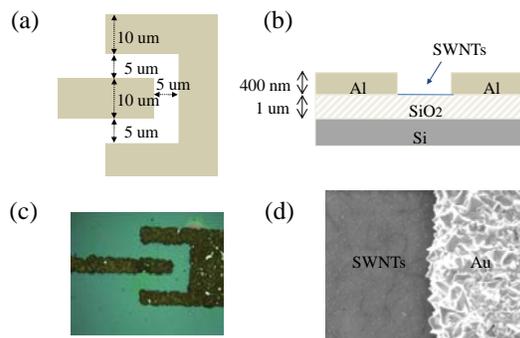


Fig. 1. (a) Semi-concentric electrode structure. (b) Cross-sectional view of the device. (c) Microscopic image of the device after Au electroless plating (ELP). (d) Scanning electron microscopy (SEM) image of the single-walled carbon nanotubes (SWNTs) deposited on the device.

Carbon nanotube biosensors were constructed as shown in Fig. 1. A 1000 nm thick tetra-ethyl-ortho-silicate (TEOS) oxide layer was deposited on the silicon wafer using chemical vapor deposition (CVD), followed by a 400 nm thick aluminum (Al) metal that was sputtered and patterned as the source/drain electrode. It is compatible with the conventional CMOS process so its structure can easily be incorporated to existing CMOS circuits. The device geometry was varied with the spacing between the source and drain electrode ranging from 5 to 20 μm , and the channel width ranging from 77 to 106 μm . To improve the contact resistance between the metal electrodes and the SWNTs, yet without the need of the additional mask, an electroless plating (ELP) can be adopted. In our case, gold (Au) was electrolessly plated on the Al electrodes using palladium (Pd) as a catalyst. The 0.05 g SWNTs were immersed in 1L 1,2-dichlorobenzene undergoing wet-oxidation to introduce defects such as carboxylic acid on the surface of the SWNTs followed by ultra-sonication for dispersion and were spread on the substrate using the dip-coating method. SEM image revealed the deposited SWNTs are 1.6 μm long with diameter of 1.4 nm on average. Fig. 2 shows the change in 2-terminal resistance before and after Au electroless plating [3].

Thereafter, electrical pulses of 10 V were applied through the electrodes to reduce the contact resistance [4]. Fig. 3 shows a series of $I_{\text{DS}}-V_{\text{DS}}$ curves of SWNTs at room temperature as an electrical pulse is applied with an incremental height and fixed duration (16 msec) through electrodes. The statistics show that the 2-terminal resistance

becomes more uniform after pulse annealing compared with those before pulse was applied.

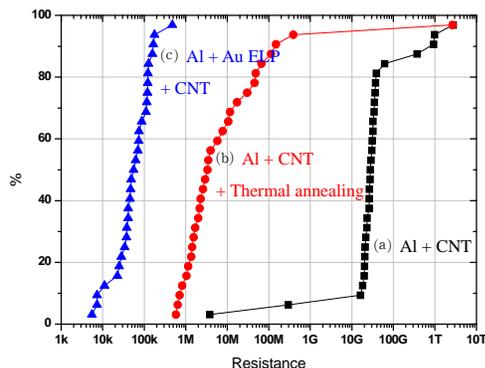


Fig. 2. Change in 2-terminal resistance (a) Resistance after SWNTs are deposited on Al electrodes. (b) After thermal annealing process. (c) After Au ELP.

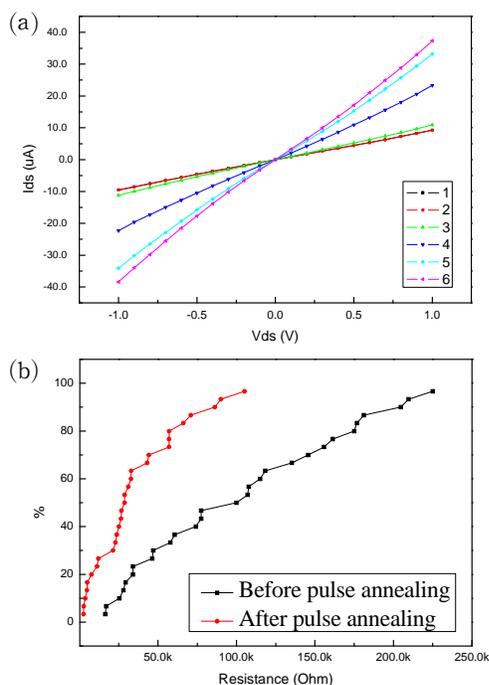


Fig. 3. (a) The evolution of the I_{DS} - V_{DS} characteristics of SWNTs with an incremental height of the applied pulse.

Curves 1–6 correspond to the following: 1 – without applying pulse, 2–after applying a pulse of 2 V for 16 msec, 3 – 4 V, 4 – 6 V, 5 – 8 V, 6 – 10 V. (b) The statistics of the changes in 2-terminal resistance after pulse annealing.

Then, SWNTs were treated with carbodiimidazole-activated Tween 20 (CDI-tween 20) which serves as a linker between SWNTs and aptamers. While the Tween-20 component which has a hydrocarbon chain in it was bound to the carbon nanotube side wall through hydrophobic interactions, the carbodiimidazole was used to covalently

attach the 3'-amine group of Aptamer. Aptamers that bind specifically to human serum albumin (HSA) were attached onto CDI-Tween 20 [5]. The electrical transfer characteristics were measured at each process stage.

The real-time measurement of conductance from HSA aptamer immobilized SWNTs were performed. First, 5 μ L droplet of diethylpyrocabonate (DEPC)-treated water was placed on the aptamer-modified SWNTs. Then, 5 μ l of

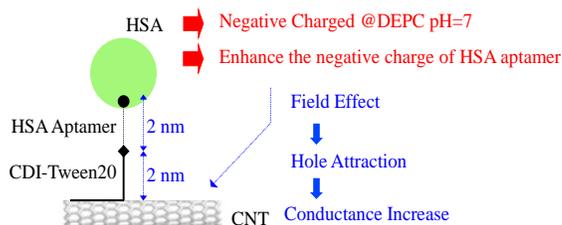


Fig. 4. Schematic diagram of binding of human serum albumin (HSA) on a aptamer immobilized SWNT-based biosensor.

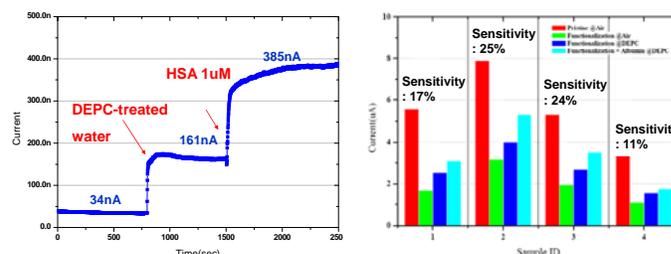


Fig. 5. (a) A real-time conductance measurement from the SWNT-based biosensor. (b) Statistics of the changes after aptamer immobilization and introducing HSA on biosensor.

HSA with concentration of 1.5 μ M was added to the DEPC-treated water droplet. In Fig. 4, we show a schematic diagram of HSA binding on HSA aptamer immobilized SWNTs.

As shown in Fig. 5a, the conductance increased as the DEPC-treated water droplet was placed. After the initial increase, addition of HSA caused the sharp increase in conductance until it reached the saturation point. Fig. 5b displays the resistance at each process and shows that the sensitivity of the aptamer-immobilized SWNTs biosensor reaches up to 25%. The HSA molecules are negatively charged in DEPC-treated water (pH 7.0), since the isoelectric point of HSA is rather low (pI 4.7). The increase in conductance after introduction of HSA could be attributed to these negatively charged HSA molecules enhancing the negative charge of HSA aptamers when the binding occurs. These negative charges are expected to give a field effect on SWNTs, thereby attracting holes in SWNTs which results in increase in conductance, while CDI-Tween 20 acts as an insulator.

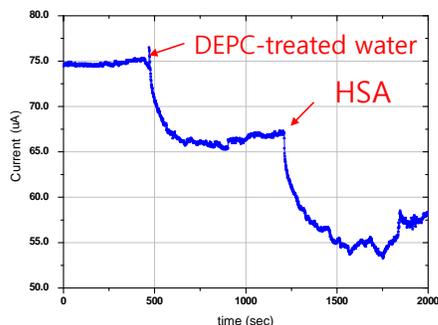


Fig. 6. Control experiment using SWNTs with no HSA aptamers attached.

As a control, we conducted the same experiment using SWNTs with no HSA aptamers attached. In this case, decrease in conductance was observed upon introducing HSA as shown in Fig. 6. This sudden drop in conductance could be explained by amine group in HSA aptamers which donates its unshared electron pair to SWNTs leading to decrease in hole concentration in SWNTs.

3 SUMMARY

We have fabricated SWNT-based biosensors, in which SWNT channels were modified with aptamers and detected human serum albumin (HSA). Aptamer modified SWNT network displayed a good performance for the detection of HSA. Our aptamer immobilized SWNT-based biosensor is a promising candidate for the development of an integrated, high-throughput, real-time biosensor. As the development and optimization studies continue, we expect that sensitive detection of numerous important bio-molecules using SWNT-based biosensors would become possible.

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