

Acid-base properties of carboxylated CNT and design of CNT-FET biosensor

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ABSTRACT

Studying of the conductance property of carbon nanotube based device led us to consider the acid-base properties of SiOH on the oxide surface and COOH on the CNT surface. We observed that the current of the carbon nanotube devices decreased continuously as time passes in the aqueous solution. The current signal is composed of two kinds of components. The first component is due to the silanol group (-SiOH) on the oxide substrate and the slow component is due to carboxyl group (-COOH) on the CNT surface. These two types of surface groups are amphoteric materials depending on the solution pH. With a simple chemical treatment for each functional group, we successfully verify the effect of the functional groups on the conductance property of carbon nanotube device. Also, through the blocking of COOH on the CNT surface, CNT characteristics becomes insensitive to the pH condition of solution. This study brings benefits to reliable operation and high sensitivity of CNTFET sensor.

Keywords: carbon nanotube, silanol group, carboxyl group, pH, field effect

1 INTRODUCTION

Various kinds of novel nanostructures have been suggested and explored for the real-time and label-free detection which can be used as the biological and chemical applications [1-2]. Among them, carbon nanotubes (CNT) are a novel class of nanomaterials that are reported to show good electrical sensitivity to the environmental conditions surrounding the transducer [3-4]. These properties are appropriate for the channel of the FET devices. Thus, the CNT-field effect transistor (-FET) has been highlighted for use in electrochemical sensor in aqueous solution. The gate of a CNTFET is often made in the liquid solution such as deionized water, or buffer solution [5]. Also in a biosensor application, unwanted chemical reactions may modulate the conductance of CNT, so that reliable operation of the sensor is not guaranteed.

In this paper, we used a carboxylated CNT-FET based sensor and analyzed the conductance property of CNTFET using a unit step-pulse voltage technique. For a CNT-FET, the SiOH group at the oxide surface and the COOH group at the CNT surface are known to be protonated or

deprotonated depending on the pH of solution [6-8]. The SiOH groups will be deprotonated and negative charged in the deionized water. Among them, the silanol groups located at the proximity to the CNT (within the electrical double layer) will cause accumulation of charge carriers in the p-type CNT and enhances CNT conductance. However, the COOH group on the CNT surface will be deprotonated in the aqueous solution, but the deprotonation of COOH can be considered as the hole-undoping by pH-sensing mechanism in the CNTFET [7]. We resolve the combination effect of SiOH and COOH groups on the CNT conductance by studying the pulse technique and applying proper materials.

2 EXPERIMENT

To achieve the CNT based electrochemical sensor, a conventional two-metal process is used to fabricate the device. The ten by ten array with 20- μm channel length is formed by the lift-off process of the gold layer. The device has a unique concentric electrode structure wherein the electrodes are composed of an inner electrode (drain) and a common electrode (source) enclosing the inner electrode. This enclosing electrode is commonly shared by all array, as shown in Fig. 1. [5]. The concentric electrode structure has salient advantages when implementing a sensor array both in the fabrication process and in the self gating effect [5]. The O₂ plasma treatment has been applied to promote the nanotube coating uniformity.

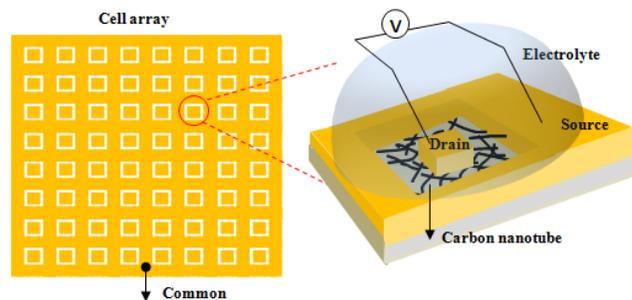


Fig.1. Schematic view of the cell array where the electrode are wired to parameter analyzer

For the channel formation between the two electrodes, the CNT network is deposited through a dip-coating process [9]. The CNTs used in our experiment are treated in HNO_3 for 30min. Depending on the measurement methods and purposes, devices are run as a real-time mode and/or an I_d - V_d mode. Amino-propyl-trimethoxy-silane (APTES), 1-(3-(dimethylamino)-propyl) - 3-ethyl carbodiimide hydrochloride (EDC), and N-hydroxy-succinimide (NHS) from Sigma-Aldrich Co. were used. All chemicals were used without further purification. To block the carboxyl group on the CNT surface, a droplet of $50 \mu\text{l}$ fresh 1mM EDC and 2mM NHS in the deionized water are placed onto the CNTFET array and washed off after 30min [10]. APTES is widely used as interfacing molecules. To modify the oxide surface of sensor array, the CNTFET was soaked in a alcohol solution containing 2% APTES for 1hr, and followed by a cleaning process at the alcohol flow [11].

3 RESULT AND DISCUSSION

Fig. 2 shows the current-voltage (I-V) characteristic curves of the pristine CNT-FET device in the deionized water. The current curves were measured with the source grounded, the drain bias swept between $\pm 0.5\text{V}$. The current decreased continuously with time. To verify that the significant current change was specific effects due to the surface functional groups such as SiOH and COOH, a unit step-pulse voltage is applied to monitor the real time change of the CNT conductance in deionized water. Fig. 3a shows the real time current change of the CNT device in the deionized water, and we observed that the current signal is composed of two components; the fast component shows a sudden increase in current instantaneously and the slow component shows a decrease in current with long time constant.

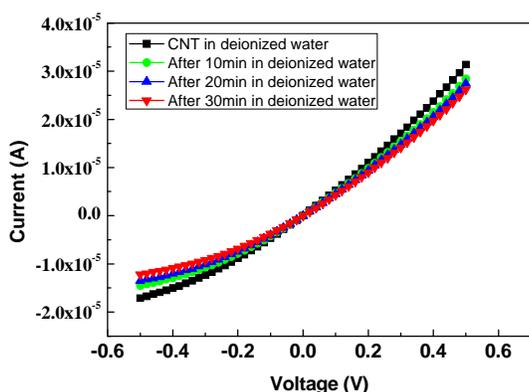


Fig. 2. I-V curves measured for a CNTFET in deionized water. After first recording of drain current, the current was continuously measured 3 times every 10min.

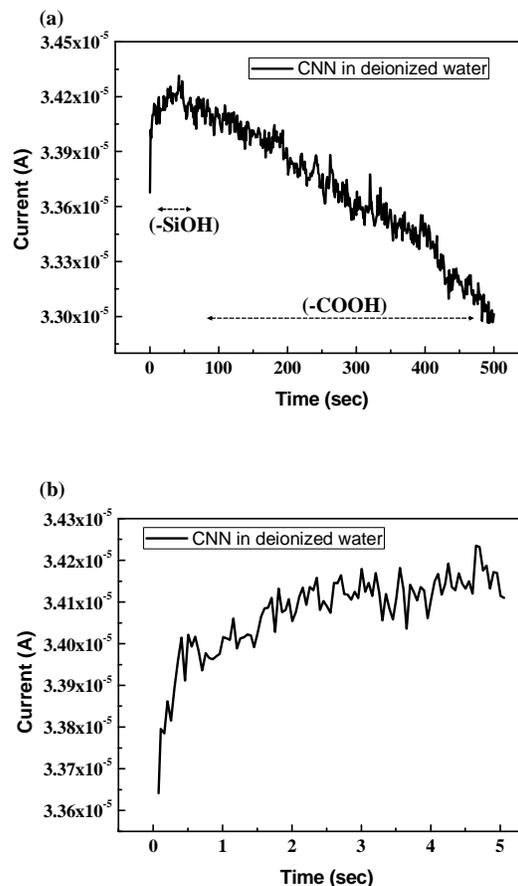


Fig. 3. Real-time measurement of current change of CNTFET (a) The conductance modulation of CNT-FET after exposure to deionized water. (b) A fast component due to the silanol groups on oxide substrate.

Fig.3b shows the increase in current (fast component), and it is analogous to typical response of an ISFET. The increase in current is explained by the field effect due to negative charged silanol group (SiOH) on the oxide surface. The silanol groups are protonated or deprotonated depending on the pH of solution. As the point of zero charge of SiO_2 is $\text{pH}_{\text{pzc}} = 3.0$ [12], the acidic silanol are likely to be deprotonated in deionized water (at $\text{pH}=6$), and their negative charges ($-\text{SiO}^-$) will cause accumulation of charge carriers in the p-type CNT and increase the current.

However, the principal problem is to transduce the recognition action of negative charged silanol group between silanol and CNT into a measurable signal. It is obvious that the charge distribution of the silanols in the vicinity of CNT plays a critical role in transferring a signal to the CNT channel. In the deionized water, counter ions are less numerous and less effective to shield the negative charge of silanol groups.

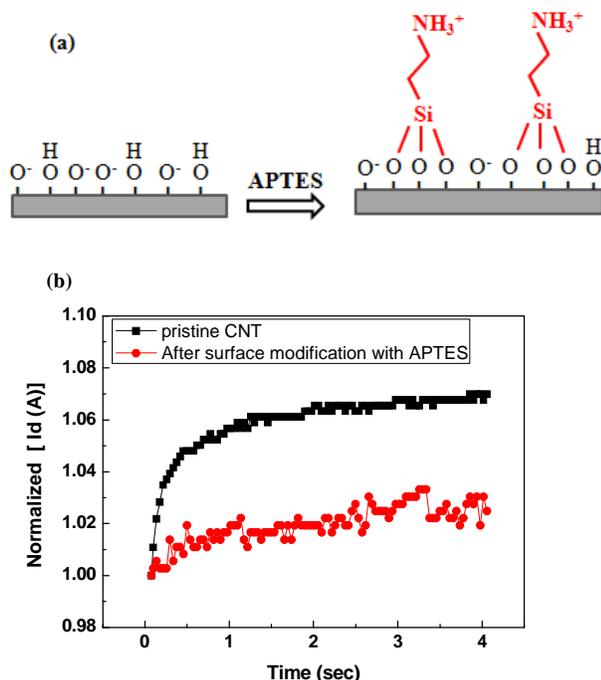


Fig. 4. (a) <A schematic of>> surface modification with APTES (b) Current>> was normalized by dividing the measured I_{SD} by the initial drain current (I_0)

Fig. 3a also shows that the decrease in current (slow component) was observed continuously with time. This result can be explained by the negative charged carboxyl group (COOH) on the CNT surface. The pH-sensing mechanism adopted in the CNT-based sensor has been generally known to be protonation / deprotonation of COOH [7]. The H^+ dissociation (deprotonation) can be considered as the hole undoping.

To verify that the conductance modulation of CNTFET is caused by these two functional groups, we carried out two supplementary experiments. First, in order to confirm that the fast component is due to silanol on oxide surface, a chemical treatment was done on oxide surface with amino-propyl-trimethoxy silane (APTES). The APTES has an amine group that will be protonated and positively charged in the aqueous solution. APTES treatment can induce the positive charged site on the oxide surface and decrease the negative net charge from the silanol groups on oxide surface as shown in Fig. 4a. After the surface modification of CNT device with APTES, we observe that the increase of current is reduced appreciably as shown in Fig. 4b, which is due to the decreasing field effect from the silanol groups.

Thus we confirmed that the fast component of current signal is due to the effect of silanol group on oxide surface.

The other experiment setup is to observe the change in the deprotonation rate of the carboxyl group by varying of hydrogen ion concentration. In general it can be stated that the deprotonation rate will be promoted by the difference between bulk pH and isoelectric pH (pH_{iep}) of COOH.

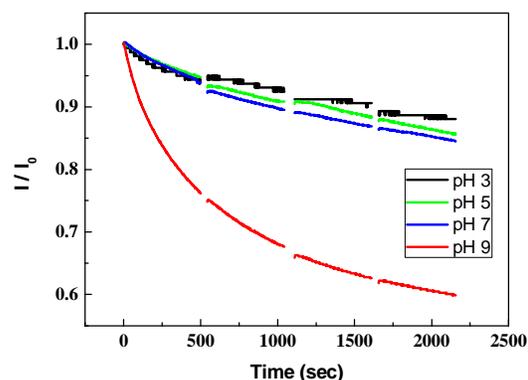


Fig. 5. The real-time current measurement of CNTFET by varying the pH value

Fig. 5 shows the real-time current measurement by varying the pH value of the buffer solution. The decrease of CNT conductance depends on the ΔpH value. We also confirmed that slow component of current signal is due to the effect of carboxyl group on CNT surface.

To suppress the effect of COOH on the CNT current, we prepared to block the COOH defect on the CNT surface. After NHS esterification between NHS and COOH on the CNT surface, a significant current decrease disappears, which indicates successful blocking of the COOH group on the CNT surface in Fig. 6.

However, this pH-dependent behavior of CNT is an undesirable side effect in a biosensor application, because the biological sensing should be performed in an aqueous phase.

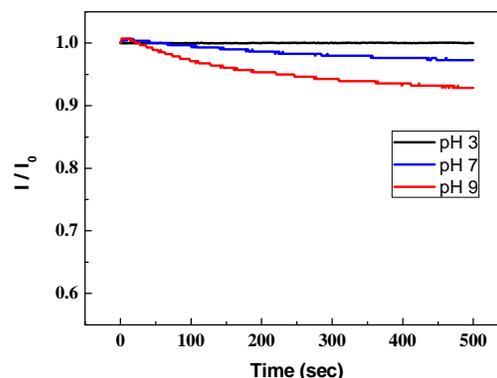


Fig. 6. The currents recorded after blocking of COOH group on CNT surface with varying the pH value. CNT device becomes insensitive to pH condition.

Thus, we suggest that blocking treatment of COOH defect on the CNT surface is promising tool for the reliable operation for the biosensor adopting the CNT as the channel.

4 CONCLUSION

We have analyzed the conductance property of the CNT FET in aqueous solution by a unit pulse measurement. Our results demonstrate that the conductance of the CNTFET was modulated by the environmental conditions surrounding the transducer such as the silanol group on the oxide surface and the carboxyl group on the CNT surface. Furthermore, we made our CNT device to be insensitive to pH condition through a chemical treatment of the CNT. As the unwanted side reactions were reduced by the surface treatments of the oxide and CNT's, reliable operation and sensitivity of the sensor may be guaranteed.

5 ACKNOWLEDGEMENT

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