Effects of Ionic Surfactant Adsorption on Single-Walled Carbon Nanotube Thin Film Devices in Aqueous Solutions

Qiang Fu, and Jie Liu

Langmuir, 2005, 21 (4), 1162-1165 • DOI: 10.1021/la047561e

Downloaded from http://pubs.acs.org on January 1, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
Effects of Ionic Surfactant Adsorption on Single-Walled Carbon Nanotube Thin Film Devices in Aqueous Solutions

Qiang Fu and Jie Liu*

Department of Chemistry, Duke University, Box 90346, Durham, North Carolina 27708

Received October 1, 2004. In Final Form: December 17, 2004

Field-effect transistors were fabricated using high-density single-walled carbon nanotube (SWNT) thin films directly grown on suitable substrates. Such approach eliminated the variations of device behaviors in individual SWNT devices by utilizing a large number of SWNTs in each device. We have found that the behaviors of such devices are closely related to the surface charge densities around SWNTs in aqueous solutions. Adsorption of ionic surfactants on the surface could significantly modulate the device characteristics, which could be detected by measuring the conductance of the devices. The devices could be tuned to be sensitive to either anionic or cationic surfactants by tailoring the surface properties of SiO$_2$ substrates around SWNTs. This effect could be potentially used to design chemical and biological sensors.

Single-walled carbon nanotubes (SWNTs) could be considered as seamless cylinders with only one layer of atoms on their walls and diameters of about 1 nm. The unique structures of carbon nanotubes enable electrons to transport along the tube axis nearly ballistically and at the same time be highly sensitive to the local environments, making them ideal candidates for nanoelectronics and chemical sensors. Chemical and biological sensors have been fabricated with SWNTs for detections in the gas phase or in aqueous solutions, showing high sensitivity to various chemicals and biological molecules. However, the electronic properties of SWNTs are very sensitive to their structures. For example, small subtle changes of the chiral angle of SWNTs could make them either metallic or semiconducting. In field-effect transistors (FETs) made of carbon nanotubes, the conductance of semiconducting SWNTs could be modulated by a gate voltage while that of metallic SWNTs could not. For applications in chemical sensors, semiconducting SWNTs are desired because of their sensitivity to environments. Unfortunately, up to now, there has been no efficient method available to produce solely semiconducting or metallic SWNTs. SWNTs synthesized normally contain nanotubes with different diameters and chiralities. Because of such random distributions in SWNT samples, the fabrication process of SWNT FETs is time-consuming and the reproducibility of devices is poor. Additionally, for sensing applications, the sensing mechanism is still not well understood, and various mechanisms for SWNT sensors have been proposed. Thus, it is very important to find a practical route to build SWNT FET devices with reproducible performance.

In one of our previous reports, by using a diblock copolymer to deliver catalyst nanoparticles on a surface, we have synthesized high-density, large-area, and uniform SWNT thin films directly on suitable substrates. Those thin films are a mixture of semiconducting and metallic SWNTs and could be used to fabricate thin film FETs. In a thin film FET, the ensemble properties of many SWNTs in each device largely eliminated the variations from individual SWNTs so that each device could perform similarly. Although large off-state current in those devices might prevent them from being used as good transistors, they are undoubtedly good candidates for chemical sensor applications since only the variation of current or conductance was measured during the detections. In this report, we show that using those SWNT thin films instead of individual SWNTs, we could fabricate reproducible chemical sensors in aqueous solutions for detecting charged molecules. We show that the characteristics of those thin film SWNT FETs were strongly affected by the adsorption of charged molecules on the SiO$_2$ substrate around SWNTs, which were considered inert for most SWNT sensor studies. By tailoring the surface properties of the SiO$_2$ substrate, we could fabricate SWNT devices that were selectively sensitive to either anionic or cationic surfactants. Our results suggest that SWNT devices in solutions are very sensitive to surface charge densities and the effect could be used to design high-sensitivity chemical and biological sensors.

The SWNT films were synthesized on a Si wafer with a 500 nm SiO$_2$ layer on top by chemical vapor deposition (CVD). Inversed micelles from diblock copolymers were used as templates to deliver high-density, uniform iron nanoclusters to the substrate as catalysts. This approach could prepare high-density, evenly distributed and mono-disperse nanoclusters in large areas without aggregation. High-density thin film SWNT films could be subsequently grown on the substrate by CVD. We then fabricated the drain and source electrodes by evaporating 5 nm of Cr and 30 nm of Au on top of the SWNT film using a 100 nm
Figure 1. (a) Scheme of using a silver wire to modulate the conductance of SWNT thin film FETs via solutions. The widths of the electrodes are 2–4 mm, the distance of the electrodes is about 100 μm, and the size of the water drop is about 25 μL. (b) A drain–source current (I_{ds}) vs gate voltage (V_g) for a SWNT thin film device (bias, 20 mV). Inset: An atomic force microscopy image of the SWNT film between the electrodes (scale bar, 500 nm).

Figure 2. (a) Drain–source current (I_{ds}) vs time when a drop of water was put on top of the devices (bias, 20 mV; V_g, 0 V). (b) Drain–source current (I_{ds}) vs time when a drop of 1 mM CTAB solution was put on top of a device wet by water (bias, 10 mV; V_g, 0 V). (c) Scheme of CTAB molecules absorbed on the surface around SWNTs in solutions. (d) Drain–source currents (I_{ds}) vs gate voltage (V_g) for a SWNT device under various conditions: (I) in water; (II) in 1 mM CTAB; (III) in 10 mM CTAB.

I_{ds} at positive V_g is about 1/3 of I_{ds} at negative V_g. The finite residue I_{ds} at positive V_g and low on–off ratio suggest that SWNT films are a mixture of semiconducting and metallic SWNTs. Obviously, the large current and small on–off ratio are not desired for transistors in which several orders of magnitude on/off ratio and small off-state current are required. However, the application of such devices as sensors is not hindered by the existence of a finite “off” current as long as the current is stable and has low noise. The detection of species is represented by the change of current rather than the absolute value of the current across the devices. Additionally, because of the high density of SWNTs across the electrode, high conductance and stable current in aqueous solutions could be obtained under relatively low bias (normally less than 20 mV). Under such low bias, the electrochemical reactions on electrodes could be avoided, and thus the contribution to conductance through the aqueous solution is negligible. Although electron hopping or tunneling through tube–tube junctions between the two electrodes may dominate the conductance, such thin film devices provided stable conductance across the electrodes and were very robust during measurements.

We have found that the characteristics of devices were closely related to the surface properties of the substrate and the chemical species in solutions. Figure 2a shows the change of the drain–source current (I_{ds}) when a drop of pure water (17.8 MΩ cm^{-1}) was dropped on top of the SWNT devices. Clearly, adding water induces the increase of the conductance across the electrodes. Such conductance increases agree with the effect of water on individual metallic SWNTs. Obviously, the large current and small on–off ratio suggest that SWNT films are a mixture of semiconducting and metallic SWNTs. However, the application of such devices as sensors is not hindered by the existence of a finite “off” current as long as the current is stable and has low noise. The detection of species is represented by the change of current rather than the absolute value of the current across the devices. Additionally, because of the high density of SWNTs across the electrode, high conductance and stable current in aqueous solutions could be obtained under relatively low bias (normally less than 20 mV). Under such low bias, the electrochemical reactions on electrodes could be avoided, and thus the contribution to conductance through the aqueous solution is negligible. Although electron hopping or tunneling through tube–tube junctions between the two electrodes may dominate the conductance, such thin film devices provided stable conductance across the electrodes and were very robust during measurements.

We have found that the characteristics of devices were closely related to the surface properties of the substrate and the chemical species in solutions. Figure 2a shows the change of the drain–source current (I_{ds}) when a drop of pure water (17.8 MΩ cm^{-1}) was dropped on top of the SWNT devices. Clearly, adding water induces the increase of the conductance across the electrodes. Such conductance increases agree with the effect of water on individual metallic SWNTs. Obviously, the large current and small on–off ratio suggest that SWNT films are a mixture of semiconducting and metallic SWNTs. However, the application of such devices as sensors is not hindered by the existence of a finite “off” current as long as the current is stable and has low noise. The detection of species is represented by the change of current rather than the absolute value of the current across the devices. Additionally, because of the high density of SWNTs across the electrode, high conductance and stable current in aqueous solutions could be obtained under relatively low bias (normally less than 20 mV). Under such low bias, the electrochemical reactions on electrodes could be avoided, and thus the contribution to conductance through the aqueous solution is negligible. Although electron hopping or tunneling through tube–tube junctions between the two electrodes may dominate the conductance, such thin film devices provided stable conductance across the electrodes and were very robust during measurements.

We have found that the characteristics of devices were closely related to the surface properties of the substrate and the chemical species in solutions. Figure 2a shows the change of the drain–source current (I_{ds}) when a drop of pure water (17.8 MΩ cm^{-1}) was dropped on top of the SWNT devices. Clearly, adding water induces the increase of the conductance across the electrodes. Such conductance increases agree with the effect of water on individual

(16) Under typical experimental conditions, the current contributed from water is less than 20 nA when 20 mV bias is applied, which contributes less than 5% of the total current.
semiconducting SWNT devices.\textsuperscript{18} However, we found that when 1 mM cationic surfactant, cetyltrimethylammonium bromide (CTAB) (Aldrich), solution was added to the devices, the conductance of the device decreased instantly (Figure 2b). Other cationic surfactants such as didodecyl dimethylammonium bromide (D TacB) (Aldrich) and poly-L-lysine (Acros) also have similar effects. More interestingly, such conductance decreases were not observed when anionic surfactant solutions such as sodium n-dodecyl sulfate (SDS) (Aldrich) were added. The different effects of anionic and cationic surfactants suggested that such changes in conductance were most likely due to the properties of the headgroups of the surfactant molecules while the chains of the surfactant had little effects.

The strong effects of cationic surfactants on SWNT conductance could be understood by considering the strong adsorption of cationic surfactant molecules on the SiO\textsubscript{2} surface. In aqueous solution (pH = 5 - 7), the SiO\textsubscript{2} surface (isoelectric point at pH = 2) is negatively charged due to the dissociation of hydroxyl groups.\textsuperscript{19} For such a negatively charged surface, cationic surfactants strongly absorb on the surface by electrostatic attractions.\textsuperscript{20} During this process, the negatively charged SiO\textsubscript{2} surface could be neutralized by the CTAB absorbed on the surface. Those absorbed CTAB molecules changed the local electrostatic environments of SWNTs and subsequently induced the conductance changes. In other words, these absorbed CTAB molecules could be considered as a molecular scale electrostatic gate and applied a positive $V_F$ to deplete the charge carriers in semiconducting SWNTs, which resulted in the decrease of the conductance (Figure 2c). Similar surface charge effects have already been applied to design high-sensitivity chemical sensors using nanowire FETs.\textsuperscript{21,22}

Such hypothesis is further supported by the $I_{ds}$ vs $V_g$ curves in different concentrations of CTAB solutions. Figure 2d shows the conductance change when $V_g$ scans from -350 to +350 mV in pure water and 1 mM CTAB and 10 mM CTAB solutions. When applying $V_g$ in pure water, the SWNT thin film acted as a typical p-type semiconductor and the $I_{ds}$ reached a depleted region when $V_g$ was above +300 mV, which suggested that all semiconducting SWNTs were depleted in this region. In 1 mM CTAB solution, the $I_{ds}$ under negative $V_g$ decreased dramatically and the $I_{ds}$ under positive $V_g$ region increased with $V_g$, and the depleted region was shifted to $V_g$ around zero. In 10 mM CTAB solutions, the $I_{ds}$ under negative $V_g$ kept decreasing while $I_{ds}$ under positive $V_g$ kept increasing. The depleted region shifted to the negative $V_g$ region while the devices acted as n-type semiconductor FETs. At zero $V_g$, such transitions agree with the effects of CTAB on the $I_{ds}$ vs time curve. The shift of the depleted region to the negative $V_g$ side with higher CTAB concentrations implies that more positive charges are absorbed on the surface when CTAB concentration increases.

Similar trends of characteristics of SWNT FETs have been observed when ammonia concentrations in solutions increased, and such transitions were attributed to the charge transfer between dissolved ammonia and SWNTs.\textsuperscript{9} However, in our experiments, this charge transfer mechanism could be ruled out because there are no free/lone-paired electrons in CTAB to donate to SWNTs. Additionally, the effects of CTAB on SWNTs are observed on all devices fabricated from SWNT thin films with various densities or diameters, which suggests that such effects are more related to surface properties around SWNTs on the substrates. We believe that electrostatic gating from the positively charged headgroups of the surfactant molecules is a more important factor in modulating the behaviors of SWNT devices. Because of the absorption equilibrium of CTAB on the SiO\textsubscript{2} surface, when the concentration of CTAB in solutions increased, more positive charges could be absorbed on the surface and cause the surface charge density to change. Those additional positive charges on the surface were then added to the actually applied $V_g$ and caused the shift of the depletion region. Although it is not clear whether the positive charge was applied directly to the SWNTs or just affected the metal–SWNT junction,\textsuperscript{5} such strong modulations of conductance of the devices by surface charges could be used to design chemical or biological sensors.

For bare SWNT devices, no obvious conductance change was observed when anionic surfactants such as SDS were added to the water drop. However, we found that the lack of response from anionic species could be easily overcome by making the SiO\textsubscript{2} surface positively charged through chemical modifications. To transform the SiO\textsubscript{2} surface to a positively charged surface, we coated our devices with poly(ethyleneimine) (PEI, MW = 25000) by immersing them in 20% methanol solution overnight.\textsuperscript{23} Such simple modifications had significant effects on SWNT device characteristics. Figure 3a shows changes of $I_{ds}$ vs time when a drop of water was added to a PEI-modified device; contrary to the unmodified devices, conductance drops rapidly when only water was added. This conductance decrease could be considered as the result of the positive charges on the PEI surface when water was added. PEI
molecules are positively charged under a wide range of pH values, which are induced by the protonation of PEI when water (pH = 6) was added. These positive charges on PEI could act as a local positive \( V_g \) to SWNTs and thus deplete the charge carriers in semiconducting SWNTs and subsequently result in conductance decreases. It is similar to the effect of CTAB absorption on unmodified devices. Figure 3b shows an \( I_{ds} \) vs time curve when 1 mM SDS is added to a PEI-coated device. Clearly, the \( I_{ds} \) increased instantly when the SDS solution was added. The effect of SDS absorption is not surprising since negatively charged SDS molecules in solutions could adsorb on the PEI surface and neutralize the positive charges. Those negative charges around SWNTs enhanced the charge carriers in semiconducting SWNTs and resulted in the increase of conductance of the p-type SWNT devices (Figure 3c). This is like a reverse process of CTAB molecules absorbed on the negatively charged SiO\(_2\) surface. Figure 3d shows \( I_{ds} \) vs \( V_g \) in pure water and in 1 mM SDS for a PEI-coated device. In pure water, the device shows that the \( I_{ds} \) vs \( V_g \) voltage is similar to that in 1 mM CTAB solution, suggesting that the surface is positively charged under such conditions. In SDS solution, the depleted region shifts to positive \( V_g \) and the \( I_{ds} \) under negative \( V_g \) increases dramatically, which is in the opposite direction from the effect of CTAB on unmodified devices. This further supports that such change in conductance of the SWNT thin film devices is due to the change in the surface charge density induced by surfactant absorption. Our results show that by simply introducing positive charges to the surface around SWNTs the devices could be depleted and introducing negative charges could enhance the conductance. Such properties of SWNT devices in solutions could be used to design and build chemical or biological sensors in aqueous solutions since a large number of chemicals and biomolecules are charged in physiological solutions.

We also found that the sensitivity of the SWNT thin film devices to those surface charge changes is very high. The detection limit could be as low as \( 10^{-8} \) M in solutions. Figure 4 shows the \( I_{ds} \) change of a typical device when different concentrations of CTAB solutions were added to the device. It clearly shows that when there is no CTAB in the solutions, adding water causes the \( I_{ds} \) to increase; 10 nM CTAB in solutions could counteract the effects from water on \( I_{ds} \). Higher concentrations of CTAB solutions cause \( I_{ds} \) to decrease. Such sensitivity is already 2 orders of magnitude higher than that of the sensors using cantilevers to detect CTAB absorption. This high sensitivity suggests that highly sensitive SWNT sensors in solutions could be built based on the sensitivity of SWNTs to surface charge changes.

In summary, we showed that using SWNT thin films instead of individual nanotubes, we could fabricate stable and robust SWNT devices with reproducible device behaviors. We showed that in aqueous solutions, such thin film SWNT devices were strongly affected by the absorption of ionic surfactants on and around the SWNTs. The surface charge density on the substrate played very important roles in affecting the electrical characteristics of the devices. We have shown that unmodified SWNT devices were sensitive to the presence of cationic surfactants while the PEI-modified devices were sensitive to anionic surfactants. The results provided more insights into the sensing mechanism of SWNT sensors in aqueous solutions. By utilizing the high sensitivity of SWNTs to surface charge changes, more chemical and biological sensors could be designed, and those investigations are underway in our lab.

Acknowledgment. The project was supported in part by a NSF NIRT program (EEC-02-10590), a nanoscience user project at Oak Ridge National Laboratory, and a 2002 young professor award from DuPont to J.L.

LA047561E
