Complementary response of In_2O_3 nanowires and carbon nanotubes to low-density lipoprotein chemical gating

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In_2O_3 nanowire and carbon nanotube transistors were used to study the chemical gating effect of low-density lipoproteins (LDL). The adsorption of LDL on these two different surfaces was investigated, which revealed a tenfold more LDL particle adsorption on carbon nanotubes than on In_2O_3 nanowires because of hydrophobic/hydrophilic interactions. The conductance of field-effect transistors based on nanowires and nanotubes showed complementary response after the adsorption of LDL: while In_2O_3 nanowire transistors exhibited higher conductance accompanied by a negative shift of the threshold voltage, the nanotube transistors showed lower conductance after the exposure. This is attributed to the complementary doping type of In_2O_3 nanowires (*n* type) and carbon nanotubes (*p* type). © *2005 American Institute of Physics*. [DOI: 10.1063/1.1881783]

One-dimensional nanostructures, such as metal-oxide nanowires and carbon nanotubes, are attracting considerable attention due to their superior sensing performance, and many applications have been demonstrated in several fields such as toxic gas sensing,[1–5] protein sensing,[6–9] and DNA sensing.[10,11] In sensing systems provided by nature, for example, the human nose, only tens of sensors are used to provide information that can be evaluated to distinguish $\sim 10^3$ different odors with the help of subsequent "pattern recognition" in the human brain.[12] Analogous to this natural approach, artificial noses can be realized using multi-sensor array connected with microprocessors. In this approach, selectivity is not obtained by special functionalization of individual sensor units but by the subsequent pattern recognition process. This technique has considerable potential for sensing in a complicated environment and has been widely utilized in commercial multi-sensor arrays. One key requirement of this approach is to gain complementary and sometimes redundant information on the effect of multiple sensors exposed to various chemicals. Inspired by this, we have studied the chemical gating effect of low-density lipoproteins (LDLs) on two nanosensing materials: In_2O_3 nanowires and carbon nanotubes. These two materials are complementary to each other, as carbon nanotube field-effect transistors (FETs) normally show *p*-type transport behavior while In_2O_3 nanowires display *n*-type semiconductor behavior. In addition, carbon nanotubes are hydrophobic while In_2O_3 nanowires are hydrophilic.

Low-density lipoprotein was chosen as the target molecule in this letter for two main reasons: (1) it is an important marker to detect individuals at risk for cardiovascular disease; specifically, coronary artery disease is the leading cause of death in the United States; (2) LDL consists of hydrophobic lipid component and hydrophilic protein component known as Apo B-100 [Fig. 1(a) inset]. LDL is the major cholesterol transport agent in human plasma. As LDL particles undergo redox reaction from the reduced form (Apo B-100 with lysine residues harboring functional NH_3^+) to the oxidized form (Apo B-100 with diene and NH_2) in the arterial wall, it initiates the development of plaque formation known as atherosclerosis.[13] The average diameter of LDL particles is 22 nm. Their lipid components are enclosed with a monolayer of about 700 hydrophobic phospholipids and the protein component is the hydrophilic apoB-100 protein.[14] We have previously reported the chemical gating effect of LDL using In_2O_3 nanowires.[9] This letter will focus on the comparative studies between carbon nanotubes and In_2O_3 nanowires. We studied the binding of LDL particles between carbon nanotubes and In_2O_3 nanowires. A tenfold difference in LDL binding was observed using atomic force microscope (AFM). More interestingly, complementary sensing responses have been observed between In_2O_3 nanowire and carbon nanotube field-effect transistors after exposure to LDL particles. Exposure to In_2O_3 nanowire resulted in an increase in conductance along with a negative threshold voltage shift while the opposite occurred with carbon nanotube

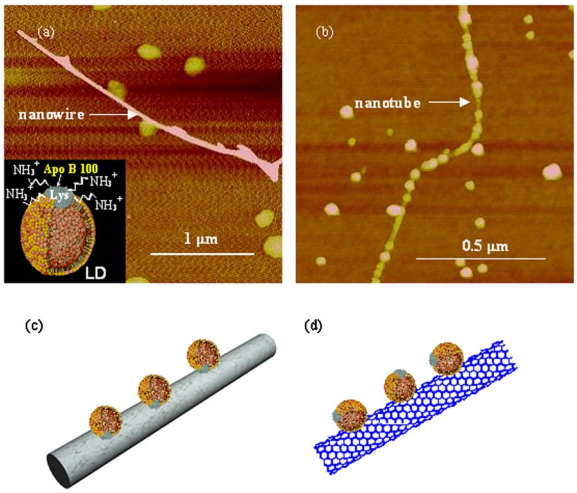

FIG. 1. (Color online) (a) AFM images of an In_2O_3 nanowire and (b) a carbon nanotube after LDL attachment. Inset: Schematic diagram of a LDL particle. (c) Schematic diagram of LDL attached to a nanowire. (d) LDL attached to a nanotube.

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based devices. We attribute this complementary sensing effect to the chemical gating effect.

In preparation for studying the chemical gating effects, initial studies on LDL particle binding to In_2O_3 nanowires versus carbon nanotubes were performed. Nanowire and nanotube suspensions were prepared by longtime vigorous sonication in isopropyl alcohol and dichloroethane, respectively. In_2O_3 nanowires were synthesized using a laser ablation process and details can be found in our previous publication.[3] Single-walled nanotubes were produced using the HiPCO (high-pressure carbon monoxide) process by Carbon Nanotechnology Inc. and used without further purification. Several drops of each suspension were spun onto clean Si substrates covered with 500 nm SiO_2, which left abundant well-separated nanowires or nanotubes atop the SiO_2 surface. Meanwhile, LDL suspension was prepared by sonicating 0.1 mg LDL particles (Sigma-Aldrich) in ~1 ml pure water (HPLC grade, VWR) for 1 h. The Si/SiO_2 substrates decorated with nanowires or nanotubes were then incubated in the LDL suspension overnight. After that, the samples were taken out of the LDL suspension, rinsed thoroughly using pure water, and blown dry under a compressed nitrogen flow.

Atomic force microscopy was subsequently utilized to carefully examine the sample surfaces. Figures 1(a) and 1(b) display two typical images of LDL adsorption on an In_2O_3 nanowire and a carbon nanotube, respectively. By using the topographic height from these images, the diameter of the nanowire and the nanotube was determined to be about 10 and 1.5 nm, respectively. This is consistent with the values obtained from the manufacturer for nanotubes and our own previous studies on In_2O_3 nanowires.[3] The lateral resolution of AFM imaging on nanoscale objects is compromised by the tip radius and is usually considered less revealing than the height information. Considerable amount of particles can be found on the sample surface after the LDL incubation, as shown in Figs. 1(a) and 1(b). The height of these particles (18 nm) is quite close to the average diameter (22 nm) of LDL,[14] therefore confirming they are indeed individual LDL particles. Further comparison between the nanowire and nanotube samples revealed different efficiency in LDL adsorption on nanotube and nanowire surfaces. In Fig. 1(a), only about 2 or 3 LDL particles can be found attached to the In_2O_3 nanowire, whereas almost the entire nanotube in Fig. 1(b) was decorated with LDL particles. An estimation of the LDL coverage density was made by counting LDL particles attached to nanowires and nanotubes found at different locations. A tenfold difference in the coverage density was derived from the estimation, with values being 1.5 LDL particles per μm for In_2O_3 nanowires and 16.3 for carbon nanotubes.

We tentatively attributed this difference in the coverage density to the hydrophilic/hydrophobic interaction between the LDL particles and the nanowires/nanotubes. The surface of LDL is known to include a small hydrophilic area made of the apoB-100 protein and a large hydrophobic area made of phospholipid molecules. Indeed data provided in the literature[14] reveal that nearly 2.3% of the surface is covered by the apoB-100 protein, while the rest 97.7% is covered by hydrophobic phospholipid molecules. According to the general principle of hydrophobic and hydrophilic interaction, hydrophobic carbon nanotubes should attract LDL particles with the phospholipid part facing the nanotube, while In_2O_3 nanowires should attract the apoB-100 part of LDL, as shown in Figs. 1(c) and 1(d). On the other hand, the difference in the nanowire and nanotube diameters should give different surface areas for this interaction to occur. As a result, the overall attachment efficiency is directly linked to the product of the active surface areas of the LDL particles and the nanowires/nanotubes. An order-of-magnitude estimate can be made by assuming the hydrophobic and the hydrophilic interactions are of similar strength, and this leads to an expected ratio of 6.4:1 between the coverage densities for nanotubes and nanowires, which is quite close to the ratio of ~10:1 determined from the AFM measurements.

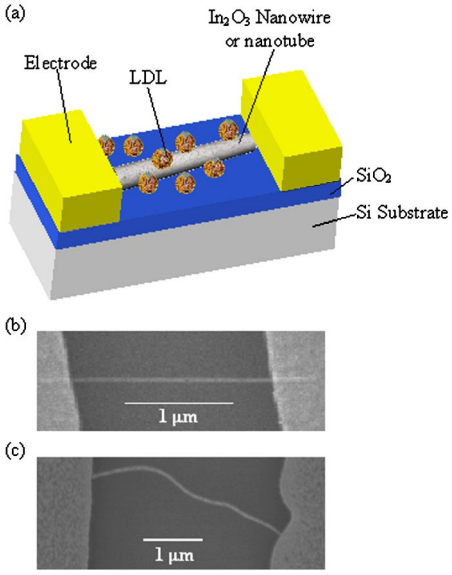

FIG. 2. (Color online) (a) Scheme for LDL adsorption on nanowire/nanotube transistors. (b) SEM image of an In_2O_3 nanowire transistor. (b) SEM image of a carbon nanotube transistor.

With increasing incubation time, more and more LDL particles were found to adsorb onto the sample surface presumably because LDL precipitated out of the suspension. Eventually a layer of LDL coated the whole surface including the electrodes after incubation for 48 h, lending a good starting point to the chemical gating studies. Figure 2(a) depicts a schematic diagram of the chemical gating experiment. An In_2O_3 nanowire or a carbon nanotube acted as the conductive channel in the field-effect transistor (FET) structure, and the substrate coated with a SiO_2 layer was used as a back gate, while the LDL deposited on the surface functioned as local chemical gates. Figures 2(b) and 2(c) display two scanning electron micrographs (SEMs) of an In_2O_3 device and a carbon nanotube device, respectively. For the In_2O_3 device, an In_2O_3 nanowire with a diameter of 30 nm was found bridging two Ti/Au electrodes with a channel length ~2 μm. The channel length of the carbon nanotube transistor is 4 μm, as defined by the photolithography process. The nanotube height is determined to be ~1.6 nm using atomic force microscopy, thus confirming it is an individual nanotube.

To ascertain the chemical gating effect, all the measurements were conducted in a vacuum chamber to avoid complexity caused by water in electrical measurement. Figures 3(a) and 4(a) show two sets of current-voltage (I-V) curves of the In_2O_3 nanowire transistor and the carbon nanotube transistor with the gate bias $V_g=0$, where conductance change in opposite directions can be clearly observed. The In_2O_3 nanowire device exhibited a zero bias resistance of

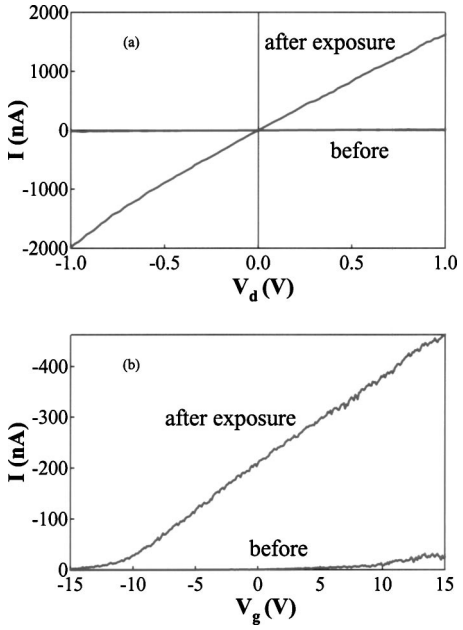

FIG. 3. (Color online) (a) *I-V* curves of an In_2O_3 nanowire device before and after exposure to LDL. (b) I-V_g curves of the same device before and after exposure. Here $V=-0.1$ V.

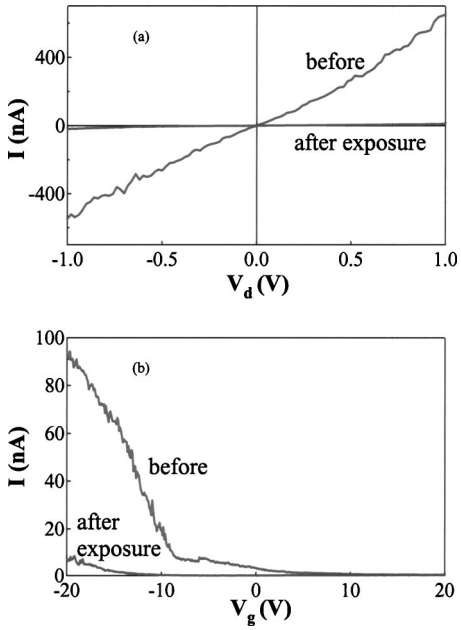

FIG. 4. (Color online) (a) *I-V* curves of a carbon nanotube transistor before and after exposure to LDL. (b) I-V_g curves of the same device before and after exposure. Here $V=0.1$ V.

0.56 MΩ after exposure, as compared to a resistance of 6.07 MΩ before the exposure. In contrast, the nanotube device showed an increase of resistance from 1.79 MΩ before the LDL exposure to 75.6 MΩ afterwards. In addition to the resistance change, the chemical gating properties of these two kinds of devices were further investigated by monitoring the dependence of the source-drain current on the gate bias. Figures 3(b) and 4(b) display two sets of I-V_g curves before and after LDL incubation, respectively. A constant drain-source bias $V=-0.1$ V was applied for the In_2O_3 nanowire device while $V=0.1$ V was used for the carbon nanotube device. A threshold voltage shift from 6.4 to -11.7 V can be derived from Fig. 3(b) for the In_2O_3 nanowire transistor. This can be converted to an increase of the electron concentration by 3.4×10^7 per cm following the widely used expression $C\Delta V_T/eL$, where C is the nanowire capacitance, ΔV_T is the shift in threshold voltage, e the electron charge, and L the channel length.[9] Similar calculations performed for the carbon nanotube device revealed a decrease of the hole concentration by 8.7×10^6 per cm after the LDL exposure, as the threshold voltage was shifted from -7.0 to -13.5 V. We attribute this effect to local chemical gating induced by the LDL particles, which led to the change of carrier concentration in both nanowires and nanotubes.[9] As a reducing agent, amino groups in apoB-100 protein may donate electrons to nanowires and nanotubes and hence increase the electron concentration in *n*-type In_2O_3 nanowires while reducing the hole concentration in *p*-type carbon nanotubes. In addition, the positive charge carried by the amino groups can also function as a positive chemical gate, thus leading to enhanced conductance for *n*-type In_2O_3 nanowires and reduced conductance for *p*-type carbon nanotubes.

In summary, we have studied the adsorption of LDL particles onto the surfaces of both carbon nanotubes and In_2O_3 nanowires. Approximately ten times more LDL particles were found to adsorb on carbon nanotubes than on In_2O_3 nanowires because of the hydrophobic/hydrophilic interactions. Chemical gating experiments performed with both nanowire and nanotube transistors revealed enhanced conductance for In_2O_3 nanowires and reduced conductance for carbon nanotube devices upon LDL exposure, which is interpreted as the local chemical gating of the amino groups on LDL particles. Our work represents a step forward toward using complementary multiple nanosensors for identifying species important for biomedical research and health care.

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