Contacting gold nanoparticles with carbon nanotubes by self-assembly

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Abstract

Single-wall carbon nanotubes (SWNTs) were functionalized with biotin at the ends and sidewalls of the nanotubes in a series of chemical reactions. Streptavidin-coated gold nanoparticles were attached to the biotin-modified SWNTs in solution in a self-assembly process. Gold nanoparticles which connected two SWNTs were selected and contacted for transport measurements. At low temperatures, Coulomb blockade oscillations were observed as a function of gate voltage. The size of the nanoparticles can be enlarged by catalytic deposition of gold leading to current increase through the SWNT–nanoparticle–SWNT junction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There is great interest in using carbon nanotubes (CNTs) in nanoelectronics, but also as sensors [1], AFM tips [2], reinforcing fibres [3], field-emission devices [4] etc. In most of these applications, it is of major importance to find a way of manipulating a large amount of CNTs, e.g. for positioning on prepatterned substrates, connecting CNTs to metallic leads or to form junctions between CNTs [5]. Several techniques were employed to orientate and deposit CNTs in a controlled way, e.g. by ac electrophoresis [6, 7], by chemical vapour deposition on a catalyst [8, 9] and by the application of surface acoustic waves to a CNT suspension [10]. An alternative route for manipulating CNTs is by chemical modification of the rather inert CNTs in order to achieve some degree of self-assembly or to incorporate some desired functionality. Such a functionalization has been reported by several groups [11], for both single-wall (SWNT) and multi-wall (MWNT) carbon nanotubes. The first attempts in this direction were mainly aimed at enhancing the solubility of CNTs in various solvents [12, 13]. Later, the attachment of functional groups for chemical and biological sensing applications [14] was also developed. The functionalization reactions can be divided into two groups: a direct addition of functional groups to the graphitic surface of the CNTs and the use of nanotube-bound carboxylic acids. These carboxylic acids are mainly induced by chemical oxidation of the nanotubes, providing a site to attach a variety of functional groups. In particular, CNTs were functionalized by thiolation which could be used to bind CNTs to metallic surfaces [15–17].

Here, we report a method which allows selective binding of gold nanoparticles to SWNTs using the biotin–streptavidin interaction. With this method, we are able to connect SWNTs via gold nanoparticles and measure the electronic transport properties of SWNT–gold nanoparticle–SWNT junctions.

2. Experimental details

SWNTs produced by laser ablation were obtained from Tube@Rice (Rice University). These tubes were first sonicated in 3:1 $H_2SO_4(96\%)$:$HNO_3(67\%)$ for 90 min following the procedure described by Liu *et al* [15]. This treatment breaks up the nanotubes and leads to the formation of carboxylic groups at the ends of the shortened CNTs and at defect sites on the sidewalls. Fourier transform infrared transmission spectra were recorded in order to verify the creation of the carboxylic groups (data not shown). The shortening of the SWNTs was verified by comparing AFM images of oxidized and non-treated nanotubes. The nanotubes were then suspended in anhydrous dimethylformamide and refluxed in thionyl chloride (Aldrich) for 24 h [18]. The resulting material was rinsed over a $0.2\ \mu$m PTFE membrane (Millipore) with anhydrous tetrahydrofuran (THF) to remove excess $SOCl_2$ and this was followed by immersion in ethylene diamine (Aldrich) for five days in order to form amine terminations. The nanotubes were then rinsed again in THF, resuspended in H_2O and reacted overnight with *N*-hydroxy succinimidyl biotin (Aldrich). After a final rinsing step, the biotin-terminated SWNTs were again suspended in H_2O and
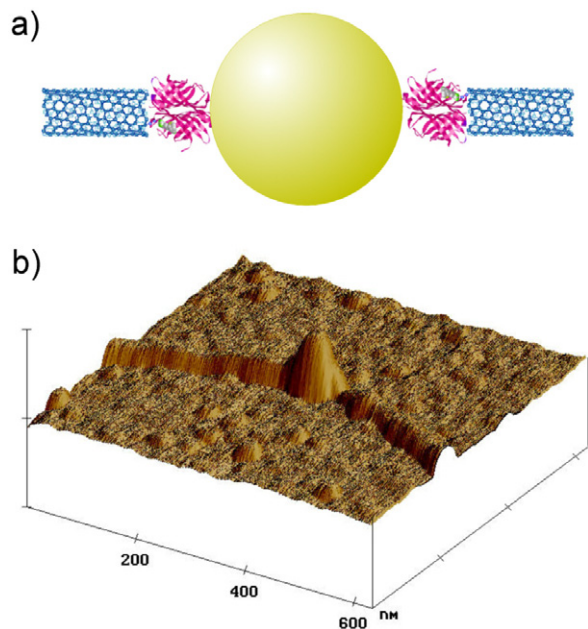
Figure 1. (a) Schematic representation of two SWNTs attached to a gold nanoparticle via streptavidin. (b) AFM image of such a SWNT–nanoparticle–SWNT junction.

Figure 2. AFM image of a single gold nanoparticle tethered to two SWNTs and contacted by gold leads.

a surfactant (sodium dodecyl sulfate) was added. The biotin–streptavidin interaction is extremely strong, allowing a stable binding of streptavidin-coated gold colloids to the biotin-terminated nanotubes simply by adding the nanoparticles to the SWNT suspension. Streptavidin is bound nonspecifically to the gold nanoparticles. The gold nanoparticles used in this study had diameters of 10 nm (Aldrich) and 25 nm (Aurion).

In order to contact SWNT–nanoparticle–SWNT structures, a drop of the suspension was applied on a highly doped silicon chip, capped with 150 nm of SiO_2 and dried. Electrical leads on top of the nanotubes were patterned by electron beam lithography, optical lithography and evaporation of titanium and gold. The structures of interest were previously located with an atomic force microscope (AFM). On the basis of the AFM images, we conclude that a large fraction of SWNTs has at least one nanoparticle attached, in most cases to one of the ends of the tube. In some cases, one nanoparticle connects two different SWNTs as shown in figures 1 and 2.

3. Results and discussion

Electronic transport measurements were carried out at room temperature and at 4 K in a cryostat. The resistances of the 14 SWNT–nanoparticle–SWNT structures measured ranged between 10 and 70 MΩ at $V_{SD} = 0.5$ V. A gate voltage can be applied to the silicon chip. In four of the six samples for which 10 nm gold nanoparticles were used, Coulomb blockade oscillations as a function of gate voltage were observed at 4.2 K. The appearance of Coulomb blockade oscillations is a typical low temperature phenomenon in systems in which a conducting island is weakly coupled to a pair of leads. As shown in figure 3, the Coulomb blockade diamonds in our system are rather complicated. White regions correspond to areas with zero conductance. The complicated patterns seem
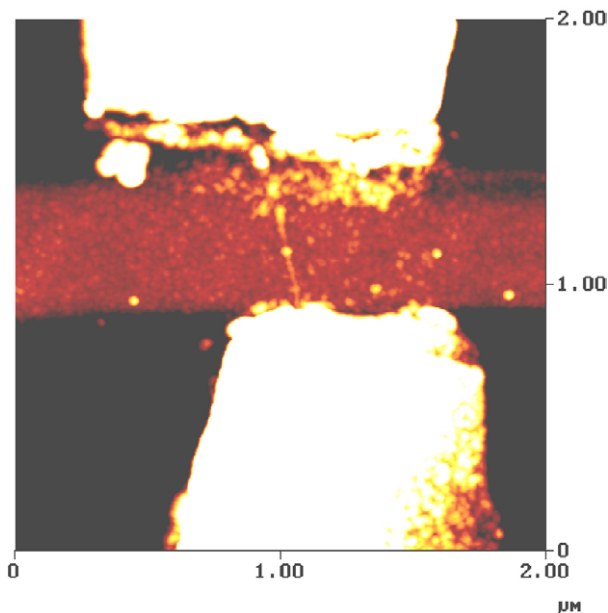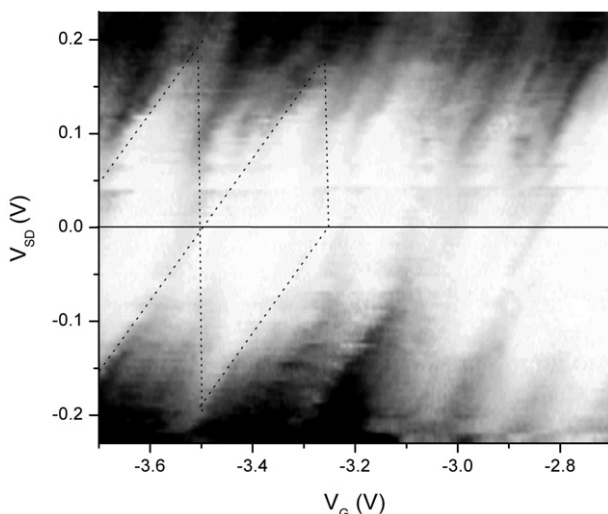

Figure 3. Greyscale plot of the differential conductance as a function of both bias voltage and gate voltage for a CNT–nanoparticle–CNT system at $T = 4.2$ K. Brighter areas correspond to low conductance. The dotted lines correspond to the Coulomb diamonds used in the analysis.

to originate from a superposition of Coulomb diamonds of different sizes and periodicity in gate voltage. This is probably due to the fact that not only does the nanoparticle act as a charged island where Coulomb blockade can take place, but also the SWNT leads can show single-electron charging effects. The largest diamonds in figure 3 correspond to a charging energy of about 180 meV. Note that the role of the streptavidin in the Coulomb blockade process it is not clear, since it is not known whether the streptavidin is removed during lift-off after lithography.

The charging energy $E_C = e^2/2C_S$ of the gold particle can be estimated using the self-capacitance $C_S = 2\pi\varepsilon_0\varepsilon_r D$
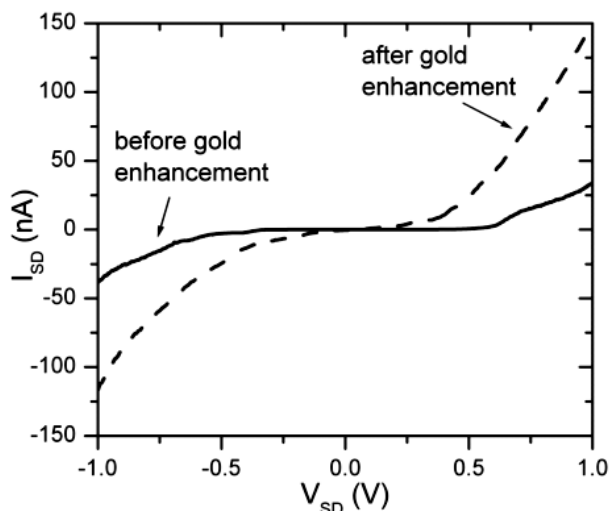
Figure 4. Variation of the current with source–drain voltage for a CNT–nanoparticle–CNT system at $T = 4.2$ K before (full curve) and after (broken curve) catalytic deposition of gold.

4. Conclusion

The results in this investigation demonstrate that SWNTs can be connected via gold nanoparticles in a self-assembly process in solution. This represents a step towards the goal of building complex electronic circuits with carbon nanotubes by providing them with molecular recognition properties. In principle, this concept could be extended to more sophisticated nanotube hybrid structures by using magnetic, semiconducting or superconducting nanoparticles. Nevertheless, the use of carbon nanotubes as metallic leads in electronic circuits will require an effective method allowing separation of metallic from semiconducting carbon nanotubes.

Acknowledgments

of a sphere with diameter $D = 10$ nm [19]. Taking into account that the average dielectric constant of the gold particle environment is $\varepsilon_r \approx 2$, we can calculate a charging energy of the nanoparticle of $E_{C,NP} \approx 140$ meV, in reasonable agreement with the measured value [20]. The self-capacitance of the SWNT leads can be evaluated with $C_S = 2\pi\varepsilon_0\varepsilon_r L/\ln(2z/d)$, where d and L are the diameter and the length of the SWNT portions which form the Coulomb blockade islands and $z = 150$ nm is the gate oxide thickness [20]. In the case shown in figure 3, $d \approx 1.5$ nm and the lengths of the SWNTs between gold nanoparticle and contacts are 500 nm respectively. The charging energy of the SWNTs can be estimated to be $E_{C,SWNT} \approx 15$ meV. However, defects inside the SWNTs can lead to additional Coulomb blockade islands of much smaller length than the SWNTs and therefore to higher charging energies. Such defects are likely to occur in the SWNTs in our system because of the chemical processes involved in the preparation. Thus, a superposition of Coulomb blockade diamonds corresponding to multiple internanotube tunnel junctions and to the gold nanoparticle is observed. Similar results were obtained for the other samples which also showed single-electron charging behaviour.

In the next step, we selectively increased the size of the gold nanoparticle in the SWNT–nanoparticle–SWNT system. This can be done by catalytic deposition of gold from a gold salt solution using a commercially available product (GoldEnhance EM from Nanoprobes). In this procedure, gold only nucleates on metallic surfaces, i.e. the nanoparticle and the contacts. After this gold enhancement treatment, the size of the gold particle increased from 10 nm to about 100 nm. As shown in figure 4, a current increase by a factor of 3–5 for $|V_{SD}| > 0.7$ V is observed upon gold enhancement. We interpret this current rise as being due to the increased overlap between the gold nanoparticle and the SWNTs on the one hand and between the contacts and the SWNTs on the other hand [21]. Altogether eight samples were treated with the gold salt solution. In five of these samples, a current increase by a factor of 2–9 was observed. One sample was short-circuited and two samples showed no current increase.

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