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Layer-by-Layer Polymer Coating of Carbon Nanotubes: Tuning of Electrical Conductivity in Random Networks

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Abstract: In this work we show that the electrical conductivity and thermoelectric power of random networks of carbon nanotube (CNT) films can be tuned by means of a layer-by-layer polymer coating technique of the individual nanotubes. Using this approach, nanotubes dispersed in water are coated before the formation of the film, achieving a control of the transport properties independent of the substrate. Below a certain temperature the conductivity departs from the ohmic behavior and enters a tunneling regime with an energy barrier for electron transport determined by the width of the polymer layer. The excellent control over the conductivity and the possibility of using the polymer coating as a gate dielectric material could be an important step for the development of an easy and scalable approach for the fabrication of CNT-based thin film transistors.

Introduction

Carbon nanotubes (CNTs) have been extensively investigated since their discovery,[1] due to their exceptional mechanical and electrical properties.[2,3] Particularly interesting is the high electronic mobility at room temperature in single-wall carbon nanotubes (SWCNTs),[4] which opened the possibility to the fabrication of field-effect transistors (FET) using individual SWCNTs.[5] However, in order to increase the current density many individual CNTs must be aligned between the source and the drain. Although some methods have been developed to produce micrometer-size films of CNTs aligned on a substrate,[6−8] they are still too complicated to be exploited commercially. Another alternative could be the use of random networks of CNTs.[9,10] They keep the large mechanical flexibility, multiple interconnecting paths, etc. that make CNT films interesting but are easy to produce and integrate at a larger scale. When they are used as the conducting channels in FET, low-density networks show large on/off ratios and moderate mobility, although there are some problems with reproducibility, especially close to the limit of percolation. Increasing the density does increase the mobility and averages out the sample dependence but reduces the on/off ratio considerably due to the increase in the portion of metallic tubes that form continuous paths between the source and drain. Therefore, there has been great interest in the development of extrinsic methods to control the electrical conductivity of dense films of random CNTs, in order to develop applications in flexible electronics.[11−13]

Herein we show that the conductivity of a random network of CNTs can be controlled by polymer wrapping of the individual nanotubes before the formation of the film. A precise tuning of the electrical conductivity can be achieved by controlling the thickness of the homogeneous CNT polymer coating by means of the so-called layer-by-layer (LbL) self-assembly technique,[14] which results in a precise control of the tube-to-tube distance. These films can be easily peeled off from the original substrate and subsequently deposited on a desire surface. Moreover, this method permits the control of the transport properties of the film without additional functionalization of the substrate usually needed in other approaches comprising the use of CNTs. Moreover, it must be applicable to SWNTs and multiwalled CNTs and opens an interesting alternative to the deposition of a polymer layer as a dielectric film between the gate and the channel in CNT-based plastic devices.[15]

The wrapping-based functionalization of the CNT is made possible because of the thermodynamic preference for the

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(1) Iijima, S. *Nature (London)* **1991**, *354*, 56.
(2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
(3) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(4) Fuhrer, M. S.; Kim, B. M.; Durkop, T.; Brintlinger, T. *Nano Lett.* **2002**, *2*, 755.
(5) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49.
(6) Lemieux, M. C.; Roberts, M.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. *Science* **2008**, *321*, 101.
(7) Lay, M. D.; Novak, J. P.; Snow, E. S. *Nano Lett.* **2004**, *4*, 603.
(8) Hone, J.; Llaguno, M. C.; Nemes, N. M.; Johnson, A. T.; Fischer, J. E.; Walters, D. A.; Casavant, M. J.; Schmidt, J.; Smalley, R. E. *Appl. Phys. Lett.* **2000**, *77*, 666.
(9) Snow, E. S.; Novak, J. P.; Campbell, P. M.; Park, D. *Appl. Phys. Lett.* **2003**, *82*, 2145.
(10) Artukovic, E.; Kaempgen, M.; Hecht, D. S.; Roth, S.; Grüner, G. *Nano Lett.* **2005**, *5*, 757.
(11) Kotov, N. A.; Dekany, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065.
(12) Engel, M.; Small, J. P.; Steiner, M.; Freitag, M.; Green, A. A.; Hersam, M. C.; Avouris, P. *ACS Nano* **2008**, *2*, 2445.
(13) Tsai, T. Y.; Lee, C. Y.; Tai, N. H.; Tuan, W. H. *Appl. Phys. Lett.* **2009**, *95*, 013107.
(14) Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao, Z. *Nano Lett.* **2009**, *9*, 2526.
(15) Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao, Z. *Nano Lett.* **2009**, *9*, 2526.

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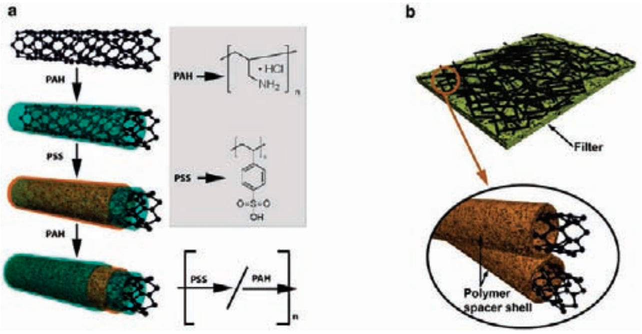
Scheme 1. (a) Illustration of the Synthetic Process Comprising the Individual CNT Functionalization using PAH as a Polymer Wrapping Agent Followed by a Sequential Deposition of Oppositely Charged Polyelectrolytes (PSS/PAH) through the LbL Self-Assembly Technique and (b) the Latter Solution after Filtration and Formation of the Film of CNT on a Cellulose Filter Substrate[a]



[a] The tube-to-tube distance in the film is determined by the number of layers previously deposited onto the CNT.

CNT−polymer interactions over the CNT−water interactions, thereby suppressing the hydrophobic surface of the CNT. Indeed, following a similar strategy and using charged polyelectrolytes as wrapping agents, we have previously shown, on the basis of electrostatic forces, the effective fabrication of CNT−inorganic hybrid materials through a controlled deposition of previously synthesized nanoparticles of different nature (metallic, magnetic, or semiconductor)[16−18] and size (spherical, rods, or dendritic).[16,19,20] However, in this work the challenge was to adjust the nanotube−nanotube distance, carried out through the alternating adsorption of monolayers of polyelectrolytes attracted to each other by electrostatic and van der Waals interactions (LbL self-assembly technique), which offers an unprecedented control over the thickness of the polymeric layer surrounding each nanotube.

Scheme 1 summarizes the experimental procedure for the formation of the CNT films, which involves two main steps. First, the fabrication of the films comprises the functionalization of well-redispersed CNTs and subsequent LbL deposition of the desire polymer layers (Scheme 1a). The nanotubes were first individually wrapped with a positively charged polyelectrolyte (polyallylamine hydrochloride, PAH), which has been shown to adsorb on CNT as a result of suppression of their hydrophobic surface,[21] followed by the assembly of a negatively charged polyelectrolyte (polystyrene sulfonate, PSS). Thus, the desired polymer thickness shell was obtained through the sequential deposition of several polymer layers (samples composed of CNTs covered with one to seven layers of polymer were synthesized for this study).

Experimental Section

Multiwalled carbon nanotubes (Nanolab) were dispersed in ultrapure water ($18\ \mathrm{M\Omega}$ cm) by following a published procedure.[17] Briefly, CNTs were dispersed in a 1 wt % aqueous solution of positively charged polyallylamine hydrochloride (PAH, 0.5 M NaCl) up to a concentration of 136 mg/L. A combination of rapid stirring and sonication was used to ensure the presence of well-dispersed, individual nanotubes in the dispersion. Excess PAH was removed by three centrifugation cycles and redispersion cycles, spinning at 9000 rpm for 12 h and redispersing in pure water by stirring and briefly sonicating. It is worth pointing out that this CNT wrapping strategy represents a noncovalent functionalization, as opposed to defect and covalent side-wall functionalization. This polymer wrapping approach is a well-known technique based on the thermodynamic preference of CNT−polymer interactions over CNT−water interactions.[22] Since this strategy represents a noncovalent interaction, new chemical bonds between the polymer and the CNT are not expected. This in principle should prevent the disruption of the intrinsic nanotube sp^2 structure conjugation, keeping intact the CNT electronic structure.

After the PAH-wrapped CNTs dispersed in water were obtained (50 mL), they were mixed with a 200 mL (2 wt %) aqueous solution of a negatively charged polyelectrolyte, poly(sodium 4-styrenesufonate) (PSS, 0.5 M NaCl). To ensure a homogeneous coating of individual and well-dispersed nanotubes, the PAH-wrapped CNT solution was added drop by drop to the PSS solution with sonication and was kept for 1 h on a rolling engine with sonication for 5 s every 10 min. Then, CNTs coated with two polymer layers, CNT/PAH/PSS, were obtained through three washing cycles by centrifugation and redispersion in pure water. Following the LbL approach and the same experimental condition explained above, the CNTs were coated with the desired thickness by a sequential deposition of oppositely charged polyelectrolytes (PAH and PSS). Thus, nanotubes coated with one, two, three, five, and seven layers were obtained.

For nanotube film formation we employed a cellulose acetate filter membrane (0.45 μm pore size). Five milliliters of a dispersion containing 0.040 mg/mL of CNTs coated with one, three, five, and seven polymer layers, respectively, for the different samples prepared were injected by means of a commercial syringe through the filter. Subsequently the filter was separated from its plastic support after the remaining water was removed by passing air trough it, in order to avoid the disruption of the film uniformity.

TEM images were obtained using a JEOL JEM 1010 transmission electron microscope operating at an acceleration voltage of 100 kV. HRTEM, STEM, and elemental mapping by XEDS analysis were carried out with a JEOL JEM 2010F transmission electron microscope operating at an acceleration voltage of 200 kV.

Thermoelectric Power Measurements. To measure the thermoelectric power as a function of temperature, a 5 × 1 mm piece of the film was mounted on a thermal insulating fiberglass fiber. Several films coming from three different samples for each step[23] were investigated, evidencing the reproducibility of the measurements. A small heater was attached to one end of the film with a thermally conductive epoxy (electrically insulating 2763 Stycast), while a piece of copper at the other end (heat drain) made a contact to the cryostat. The temperature gradient and voltage drop across the film was measured with type E thermocouples arranged in series

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(16) Correa-Duarte, M. A.; Sobal, N.; Liz-Marzan, L. M.; Giersig, M. *Adv. Mater.* **2004**, *16*, 2179.

(17) Correa-Duarte, M. A.; Grzelczak, M.; Salgueirino-Maceira, V.; Giersig, M.; Liz-Marzan, L. M.; Farle, M.; Sierazdki, K.; Diaz, R. *J. Phys. Chem. B* **2005**, *109*, 19060.

(18) Grzelczak, M.; Correa-Duarte, M. A.; Salgueiriño-Maceira, V.; Giersig, M.; Diaz, R.; Liz-Marzán, L. M. *Adv. Mater.* **2006**, *18*, 415.

(19) Correa-Duarte, M. A.; Perez-Juste, J.; Sanchez-Iglesias, A.; Giersig, M.; Liz-Marzan, L. M. *Angew. Chem.* **2005**, *44*, 4375.

(20) Sanles-Sobrido, M.; Correa-Duarte, M. A.; Carregal-Romero, S.; Rodriguez-Gonzalez, B.; Alvarez-Puebla, R. A.; Herves, P.; Liz-Marzan, L. M. *Chem. Mater.* **2009**, *21*, 1531.

(21) Grzelczak, M.; Correa-Duarte, M. A.; Salgueiriño-Maceira, V.; Rodríguez-González, B.; Rivas, J.; Liz-Marzán, L. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7026.

(22) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265.

(23) Each step corresponds to films composed of CNT coated with an increasing number of polymer layers. Thus, films made of CNT coated with one, three, five, and seven polymer layers have been investigated.

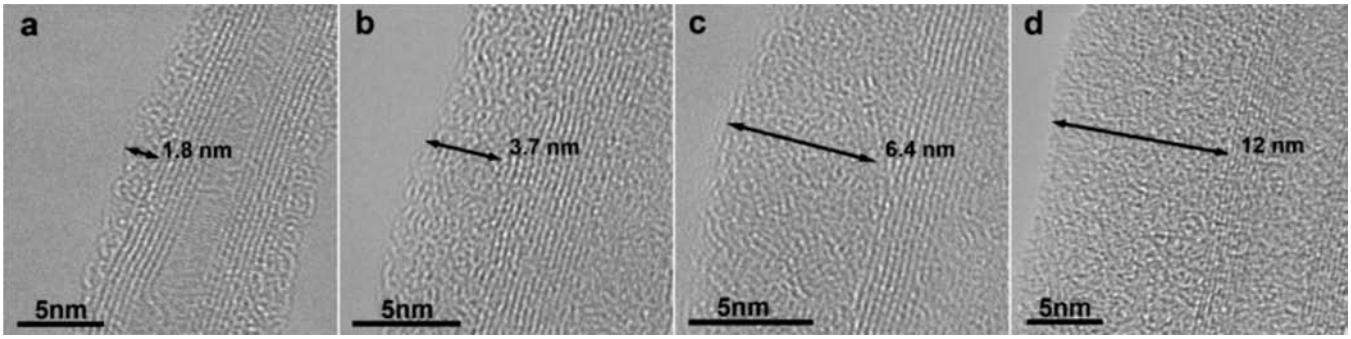

Figure 1. HRTEM images of the CNT coated with (a) one, (b) two, (c) three, and (d) seven polyelectrolyte layers, corresponding to polymer thicknesses of 1.8, 3.7, 6.4, and 12 nm, respectively. There is a very good agreement between the thickness of the polymer layer observed experimentally and that expected on the basis of the number of layers deposited.

(electrically insulated from the sample with 2763 Stycast) and two copper wires. To be sure that the thermal gradient and the voltage drop were being measured at the same place, two small Cu films were attached to the CNT film with thermally/electrically conducting silver epoxy (Dupont 4929N). The thermocouple and the voltage wires were attached to these Cu films, as shown in the inset to Figure 3. The thermal gradient and the thermoelectric voltage were monitored with a Keithley 2182A nanovoltmeter. The base temperature was changed with a continuous flow cryostat, with the sample under vacuum (10^{-5} Torr).

The thermoelectric power was determined by two independent means: after reaching a steady state through an applied current to the heater and by fitting the linear V vs ΔT response to a heating pulse. The difference between both methods and between different experiments was always lower than 5%.

Electric Resistivity Measurements. The electrical resistivity was measured as a function of temperature in a continuous flow cryostat with the sample under vacuum, from 5 K to room temperature. We used four contacts, and the voltage was monitored with a Keithley 2182A nanovoltmeter. The smallest possible current was used in order to avoid heating of the sample at low temperature.

The typical distance between the inner (voltage) contacts was 500 μm, although it was systematically varied (between 400 μm and 1 mm) in order to check the reproducibility of the experiments.

For I/V experiments a 6221 ac/dc current source and a 2182A nanovoltmeter, both from Keithley, were used.

Results and Discussion

A high-resolution transmission electron microscopy (HRTEM) examination of the polymer-coated CNT (Figure 1) shows that the polymer thickness increases, as expected, with the number of polymer layers deposited. The amorphous polymer layer surrounding each CNT is clearly distinguished from the walls of the tube. The uniformity of the coating is evidenced from the gradual increase of the thickness in 1.8 ± 0.2 nm steps per layer.

Once the CNTs were coated with the desired polymer thickness, the CNT films were obtained through a filtering strategy from the aqueous dispersions using commercial cellulose filters. Figure 2 shows the SEM images of the films obtained through this filtration approach, showing a good homogeneity and excellent control over the nanotube−nanotube distance by successive layer-by-layer polymer wrapping. The density and thickness of the films can be simply controlled by the concentration of tubes in the solution. After they are formed, the films are self-supporting and can be easily removed from the cellulose matrix by immersing them for a short time in acetone.

Summarizing this part, the polymer wrapping of CNTs through LbL and subsequent filtering introduced in this work provides random networks of CNTs in which the CNT−CNT distance, density, and thickness of the network can be easily adjusted.

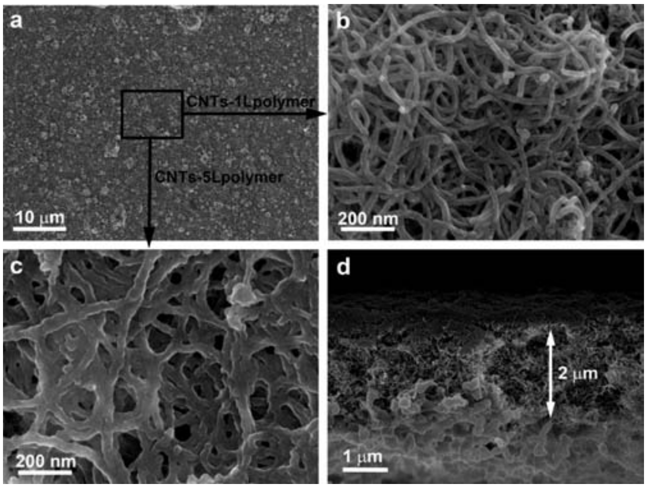

Figure 2. Representative scanning electron microscopy (SEM) (a) top and (d) cross-section views images of the CNT films. In (b) and (c) we show a comparison between two films in which the CNTs have been coated with one and five polymer layers, respectively. The same magnification was used for a direct comparison.

However, the main goal of this synthetic effort was to design a method to tune the electron transport between CNTs; therefore, we have studied the electrical conductivity and thermoelectric power in thin films of CNT wrapped with an increasing number of polymer layers. In the following we present the results for 1.5−2 μm thick, very dense films in which the only parameter to be varied is the number of polymer layers surrounding each tube.

As we indicated before, the first layer surrounding the CNT in all cases is composed of PAH, a positively charged polyelectrolyte. Although we selected an electrostatic process for not disrupting the electronic structure of the CNT, it could be possible that some charge transfer could occur between the CNT surface and the polymer, affecting the conductivity of the system. Thermoelectric power (Seebeck coefficient) could give important information in this respect, at the time that provides access to the intrinsic electrical transport properties of the nanotubes. When a thermal gradient is applied to a sample, diffusion of the charge carriers from the hot to the cold side creates a (thermoelectric) voltage when measured under open-circuit conditions (no current flow). This results in the ratio $\Delta V/\Delta T$, which defines the thermoelectric power or Seebeck coefficient, S, of the system and gives a measure of the ratio of

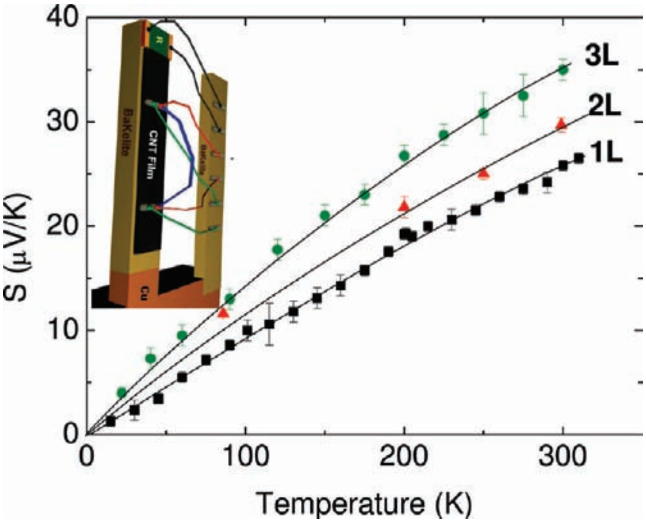

Figure 3. Temperature dependence of the thermoelectric power in different films of CNT wrapped by 1L (black squares), 2L (red triangles), and 3L (green dots) polymer layers, according to the procedure described in Scheme 1. The lines are guides to the eye. The inset shows a scheme of the sample holder designed to measure the thermoelectric power of the films, as described in the text.

electric to thermal energy conversion and vice versa. In a metallic system, the diffusion of the charge carriers is determined by the band structure around the Fermi energy, and hence, much information about the electronic band structure can be obtained from *S*(*T*).

To measure the thermoelectric power as a function of temperature, a small thermal gradient was generated and monitored along with the voltage drop, on a 5 × 1 mm piece of the film. The results are shown in Figure 3 for the films of CNT surrounded by one, two, and three layers of polymer (1L, 2L, and 3L, respectively). For the 1L film the thermoelectric power is positive (hole conduction) and increases with temperature at a rate very similar to those reported in mats of p-doped SWCNTs.[8,24]

Increasing the number of polymer layers increases the value of the thermoelectric power (about 15−20% per layer at room temperature). Although in a thermoelectric power experiment no current flows across the sample, a filtering of low-energy charge carriers at the CNT−polymer interface is expected. Actually, the growth of an insulating barrier on a metallic element is a common strategy to increase the thermoelectric power in the production of nanocomposite thermoelectric materials.[25]

Therefore, this experiment is the first confirmation of the possibility of tuning the electronic properties of films of CNTs via individual polymer wrapping, without disrupting the electronic structure of the nanotubes.

On the other hand, the electrical resistivity of a thin film of CNT with one layer of polymer (CNT-L1 (not shown) is practically temperature independent above ∼100 K, resembling bad-metal behavior. Below this temperature a thermally activated behavior is seen. Given that the length of the nanotubes is much shorter than the distance between the contacts, the increasing resistance at low temperatures must be related to an energy barrier for the process of charge transfer from tube to tube. In order to explore this behavior, we have measured the *I*/*V* curves of the film at different temperatures, from 5 to 300 K. The results are shown in Figure 4 for the L1 film. Below ∼150 K, the nonlinear behavior is clear at low voltages; at high voltages the electric field overcomes the energy barrier and the ohmic (linear) regime is progressively recovered. The value of the non-ohmic resistance at low field can be obtained by subtracting the ohmic contribution, as follows:

$$R_{\mathrm{LV}} = G\left[\frac{\mathrm{d}V}{\mathrm{d}I} - R_{\mathrm{ohm}}\right] \qquad (1)$$

where *G* is a geometric factor related to the dimensions of the sample. The cross section of our samples is the same (1.3 mm

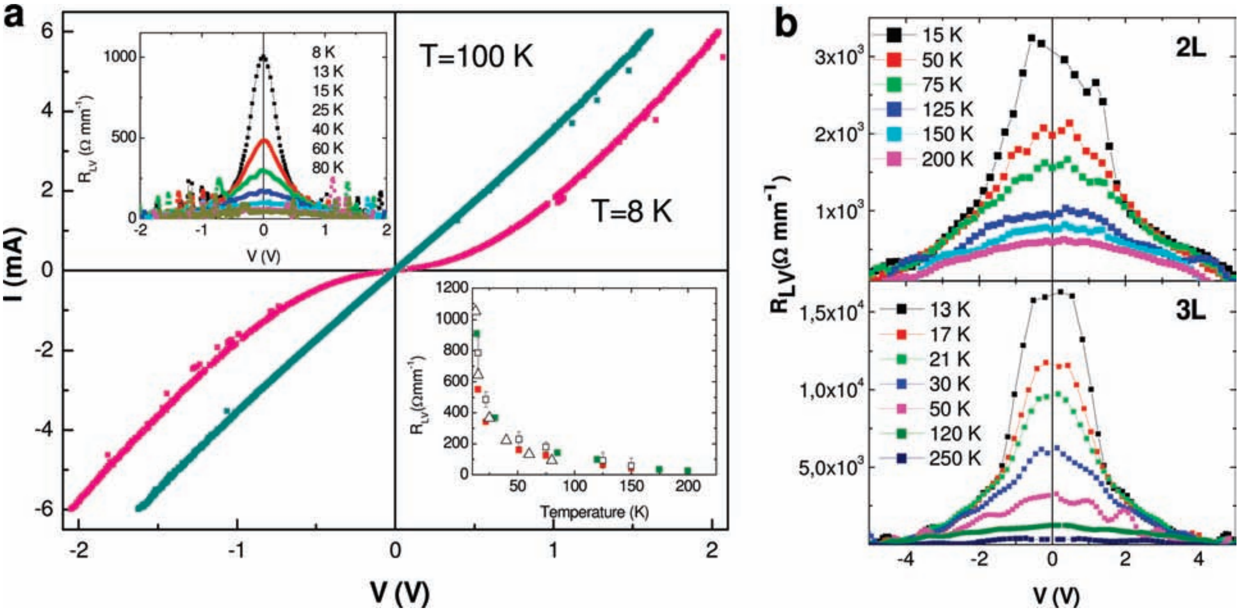

Figure 4. (a) *I*/*V* characteristics at two different temperatures for the sample with one layer of polymer (1 L). In the upper inset we show the temperature dependence of the low voltage resistance for CNT-1L (PAH), extracted from the *I*/*V* curves (see text). In the lower inset we show the temperature dependence of R_{LV} for samples with 1L of PAH (solid green) and PSS (solid red). The nature of the polymer does not affect R_{LV} as long as the thickness of the layer surrounding each nanotube remains constant. Different points (open) correspond to experiments performed by varying the distance between the electrical contacts. All the other dimensions of the films were kept constant between different experiments. (b) Low-voltage tunneling resistance for (top) CNT-2L and (bottom) CNT-3L at different temperatures obtained from the *I*/*V* curves according to eq 1.

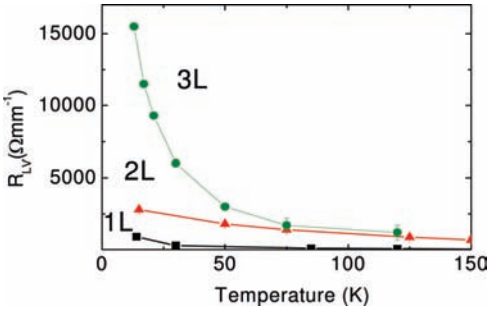

Figure 5. Temperature dependence of the low-voltage tunneling resistance in films of CNT wrapped by 1L (black squares), 2L (red triangles) and 3L (green dots) of polymer. The lines are guides to the eye.

× 1.5 μm, within the error); therefore, the different measurements have been normalized by the distance between contacts (typically between 0.4 and 1 mm). The results are shown in the inset of Figure 4 for 1L films. The low-voltage resistance, R_{LV}, decreases with temperature and is independent of the nature of the polymer surrounding the tubes as long as the intertube distance remains constant. This is demonstrated in the lower inset to Figure 4a, where we compare the results for CNT-1L covered with PAH (a polymer with positive charge density) and PSS (a polymer with negative charge density).

On the other hand, increasing the number of polymer layers surrounding the CNTs increases the resistivity of the films dramatically. The results for CNT-2L and CNT-3L are shown in Figure 4b and are summarized for the three samples in Figure 5. The nonlinear resistance at the lower temperature increases with the number of polymer layers in an exponential fashion, suggesting that electronic tunnel dominates the conductivity through the insulating polymer layer at low temperature. We have attached thermocouples to the film in order to discard any temperature-related artifacts due to the increasing current. Then, the low voltage resistance at low temperatures can be associated to a tunneling resistance due to the energy barrier imposed by the polymer layer to the intertube charge transfer. At higher temperatures thermal energy overcomes the energy barrier, recovering the linear regime. This effect can be controlled through the CNT−CNT distance: R_{LV} is practically zero above 150 K in 1L but remains on the order of 250 Ω mm^{-1} in 3L at 300 K. Increasing more the number of layers dramatically increases the resistivity, making it impossible to follow the temperature dependence in a wide range below room temperature.

Therefore, the method presented here constitutes a valid tool for tuning the conductance of random CNT films in a wide temperature range, which is applicable to SWCNTs and MWCNTs.

This method of control of the conductivity opens new opportunities for the use of dense networks of random CNTs in plastic electronics. In particular, we think this approach could provide a more efficient way to integrate a homogeneous polymer layer as an efficient and flexible dielectric between the gate and the nanotube network in field effect transistors.

Conclusions

In summary, we have described a chemical method to wrap individual CNTs with a given number of polymer layers. Through a posterior filtering strategy we have demonstrated the possibility of making homogeneous films of coated CNTs in which the distance between tubes is determined by the number of polymer layers surrounding each individual tube. Electrical conductivity and thermoelectric power experiments at different temperatures show that charge filtering at the interface barrier provides an effective method to tune the electrical conductivity in these films. We also think this method could be exploited in the fabrication of plastic transistors, by adjusting the dielectric properties and thickness of the polymer film.

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(24) Romero, H. E.; Sumanasekera, G. U.; Mahan, G. D.; Eklund, P. C. *Phys. Rev. B* **2002**, *65*, 205410.
(25) Martin, J.; Wang, L.; Chen, L.; Nolas, G. S. *Phys. Rev. B* **2009**, *79*, 115311.