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Quantitative Conductive Atomic Force Microscopy on Single-Walled Carbon Nanotube-Based Polymer Composites

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S Supporting Information

ABSTRACT: Conductive atomic force microscopy (C-AFM) is a valuable technique for correlating the electrical properties of a material with its topographic features and for identifying and characterizing conductive pathways in polymer composites. However, aspects such as compatibility between tip material and sample, contact force and area between the tip and the sample, tip degradation and environmental conditions render quantifying the results quite challenging. This study aims at finding the suitable conditions for C-AFM to generate reliable, reproducible, and quantitative current maps that can be used to calculate the resistance in each point of a single-walled carbon nanotube (SWCNT) network, nonimpregnated as well as impregnated with a polymer. The results obtained emphasize the technique's limitation at the macroscale as the resistance of these highly conductive samples cannot be distinguished from the tip-sample contact resistance. Quantitative C-AFM measurements on thin composite sections of 150–350 nm enable the separation of sample and tip-sample contact resistance, but also indicate that these sections are not representative for the overall SWCNT network. Nevertheless, the technique was successfully used to characterize the local electrical properties of the composite material, such as sample homogeneity and resistance range of individual SWCNT clusters, at the nano- and microscale.

KEYWORDS: quantitative, conductive-atomic force microscopy, carbon nanotubes, polymer composite, conductive nanocomposites

INTRODUCTION

Atomic force microscopy (AFM) is a popular technique for characterizing the surface of materials because it brings the advantage of providing three-dimensional topography information with a vertical resolution of less than 1 nm combined with, usually, a greater level of detail than electron microscopy techniques. AFM uses a sharp tip (with a typical radius of curvature of several tens of nanometers) that is scanned over the surface of a sample, thereby generating a feed-back based on the interaction between the tip and the sample. If also a voltage is applied between a conductive tip and a conductive sample during these measurements, a current can be measured in addition to the topographic information obtained, generating a current map correlated with a topography map. This combination, named conductive-AFM (C-AFM), is a technique typically used for qualitative analysis to identify conductive paths at the surface of different materials,¹ to differentiate between areas/domains with different conductivities,^{2,3} or to correlate topographic features with their electrical properties.^{3,4}

However, quantitative C-AFM measurements are not common because of the many difficulties encountered by this technique. The electrical resistance measured via C-AFM is strongly influenced by many factors, such as the compatibility between the tip material and the sample, the tip force on the sample, the contact area between the tip and the sample, and environmental conditions such as humidity and temperature.

On top of that, all AFM tips are unique and can have variations in tip diameter or even electrical properties due to oxide layers on the conductive coating.⁵ Moreover, these tips can degrade during AFM scans because of tip oxidation or brushing-off of their conductive layer, leading to differences in current values across the same area during multiple consecutive scans. All these aspects pose a tremendous challenge for achieving reliable and reproducible quantitative C-AFM results. In an earlier study, Souier et al.⁶ approached C-AFM from a quantitative point of view for aligned multi-walled carbon nanotubes impregnated in a polymer matrix. They too obtained different results for different conductive tips as well as ohmic and nonohmic contact with the samples for Pt-coated tips.

This study comprises a systematic approach toward finding the suitable conditions for C-AFM to generate reliable, reproducible and quantitative current maps that can be used to calculate the resistance in each point of a SWCNT network, either nonimpregnated or impregnated with a polymer matrix, with nanometer resolution. The technique was also used to characterize the local electrical properties of a highly conductive composite material at the microscale as well as at the nanoscale.

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MATERIALS AND METHODS

Sample Preparation. SWCNT composite samples were prepared from free-standing 2 μm thick SWCNT films, where the CNTs occupy 61% of the film volume, as described in a previous study.⁷ These films were subsequently embedded in a polymer matrix composed of a cross-linked epoxy/amine mixture (Epikote 828 and Jeffamine D-230) using a silicone mold with the dimensions $5 \times 10 \text{ mm}^2$. These samples are referred to as (SWCNT) films and (SWCNT) composites, respectively. Two edges of the resulting bulk samples were ground to remove the excess polymer and expose the embedded composite film in order to facilitate a direct contact to the conductive composite. A pyramid shape was cut at the top of the embedded film for further ultramicrotoming. Sections with a thickness in the range of 150–350 nm were cut from the sample using an oscillating, 3 mm wide ultrasonic diamond knife (Diatome, Switzerland) with a 35° cut angle.

Resistance Measurements. In order to determine the effect of the apparent contact area between the SWCNT film and an electrode on the measured resistance, two identical Au-plated flat probes were placed on opposite sides of a free-standing SWCNT film using a custom-made system (Figure 1a). These probes were connected to a

Figure 1. (a) Custom-made system used to measure resistance across the width of a free-standing SWCNT film and (b) flat, Au-plated probes with different diameters.

VC840 multimeter (Votcraft, Germany) in order to measure the resistance across the width of the film. The diameter of these probes (Romex B. V., The Netherlands) was then systematically varied: EPA C30 ($d = 0.76 \text{ mm}$), EPA 2C 40 ($d = 1.02 \text{ mm}$), EPA 3C ($d = 1.27 \text{ mm}$), EPA 2F ($d = 1.91 \text{ mm}$), EPA 3F ($d = 2.54 \text{ mm}$), and EPA 4F ($d = 3.96 \text{ mm}$) (example in Figure 1b).

To determine the effect of the distance between the electrodes on the measured resistance of the SWCNT film, we placed two identical probes with $d = 2.54 \text{ mm}$ on the same side of the SWCNT film and the distance between them was systematically varied.

C-AFM Measurements. AFM measurements were performed using a SOLVER NEXT (NT-MDT, Russia) for the free-standing SWCNT film and the composite sections. The bulk composite sample was measured using a NTEGRA-Tomo device (NT-MDT, Russia) based on a NTEGRA SPM (scanning probe microscopy) platform integrated with a Leica UC6NT ultramicrotome.⁸ This construction allowed the investigation of the sample surface by AFM directly at the cross-section of the composite film before and after removing at least 2 μm of material from the surface of the sample by sectioning. The measurements were done either in air ($\text{RH} > 50\%$) or in a controlled humidity environment. The humidity (and air composition) was varied by flushing nitrogen at a slow rate inside the sample chamber. The samples were kept under the chosen conditions for several hours before C-AFM measurements were done for the system to stabilize (temperature range of $20\text{--}24^\circ\text{C}$ and relative humidity $\text{RH} \pm 2\%$). Silicon tips from NT-MDT coated with Au and Pt (CSG01, force constant $k = 0.003\text{--}0.13 \text{ N/m}$), W_2C (HA_HR, $k = 17\text{--}43 \text{ N/m}$), TiN (NSG01, $k = 1.45\text{--}15.1 \text{ N/m}$) and conductive, doped diamond (DCP01, $k = 2.5\text{--}10 \text{ N/m}$) were tested as well as PtSi-coated tips from Nanoandmore GmbH (PtSi-FM-10, $k = 0.5\text{--}9.5 \text{ N/m}$).

The initial SWCNT film deposited on a glass substrate, was connected to the conductive stage via a Au wire placed on the surface of the film. C-AFM measurements were done at a distance of $\approx 1 \text{ mm}$ away from this wire. The bulk composite sample was sputtered with Au using an Emitech K550 sputter coater at 20 mA current for 2 min, to facilitate the electrical contact between the embedded conductive composite and the sample holder. The composite sections were

deposited on Au-coated monocrystalline silicon wafers and the connection between the Au layer and the stage was also done via a Au wire. Therefore, the second electrode, the tip being the first, is Au for all samples measured.

RESULTS AND DISCUSSION

Selecting the Conductive-AFM Tip. Selecting a suitable tip for C-AFM is an essential task in terms of compatibility between the tip material and the sample to be measured. Different metals can lead to various contact resistances with SWCNTs. Matsuda et al.⁹ calculated that the strongest bonding between a graphene layer and a metal is for Ti, followed by Pd, Pt, Cu, and Au, with Pd-SWCNT contacts having a 9 to 52 times higher contact resistance than Ti-SWCNT contacts. In addition, SWCNTs are usually a mixture of different metallic and semimetallic tubes and therefore there are contact resistance variations due to the type of the tubes alone. To make the matter even more complicated, the contact resistance between the tip and the sample $R_{\text{C_tip-sample}}$ can rarely be separated from the contact resistance between the second electrode (substrate/wire) and the sample $R_{\text{C_subs/wire-sample}}$. These two are usually measured together as the total contact resistance between the two electrodes (tip and substrate/wire) and the sample as described by

$$2R_{\text{C}} = R_{\text{C_tip-sample}} + R_{\text{C_subs-sample}} \quad (1)$$

The two-terminal contact resistance between different types of metal electrodes and SWCNTs can vary from several $\text{k}\Omega$ to several $\text{M}\Omega$,^{9–12} with metallic tubes giving the lowest values in the range. Our samples are SWCNT networks, as-prepared and impregnated with a polymer, which contain a mixture of metallic and semimetallic tubes. The second electrode (next to the tip) is Au, whether sputtered on the substrate, directly on the sample or simply a Au wire in contact with the sample. This means that the tip has to be conductive enough to handle a wide range of current variations for the same scanning area.

A series of different conductive tips coated with Au, Pt, W_2C , PtSi, TiN, and doped diamond were compared in terms of resistivity, radius of curvature and hardness and tested on the initial SWCNT film (detailed results are presented in the Supporting Information). Results showed that the Au-coated tips are soft and easily damaged during consecutive scans even at low contact forces. Tips coated with W_2C and TiN gave a Schottky barrier type of contact and inconsistent results, respectively. PtSi tips gave ohmic contacts with both Au substrates and the SWCNT films and consistent results for different tips. Moreover, these tips have a low resistivity, a reasonable hardness and the lowest radius of curvature out of all tips tested (Table S1). Therefore, these tips were chosen as most suitable and were further used for all for our C-AFM measurements.

Selecting the Contact Force. The contact force can have a strong influence on the contact resistance between the tip and the sample.^{13,14} This is either due to the penetration of the water/adsorbents layer at the surface of the tip and substrate, or to the increased contact area that results from a higher contact force. For comparison, scanning spreading resistance microscopy (SSRM) techniques use contact forces higher than 1000 nN in order to ensure that the measured resistance is dominated by the spreading resistance and not by the contact resistance.¹⁵ Bietsch et al.¹⁴ showed that Pt-coated tips on a Au substrate gave reproducible current behavior only at forces higher than 300 nN. On the other hand, a contact force of 150

nN also proved to be sufficient in order to establish ohmic contact and a stable current flow between a W_2C tip and a Au substrate.¹³

However, Au surfaces are relatively flat compared to SWCNT films where the radius of the tube and not the radius of the much larger tip determines the contact area. Because of the nanosized contact area between the tip and SWCNTs, the tip-tube pressure is much larger than the tip-flat surface pressure for the same contact force. de Pablo et al.¹⁶ showed that, once an electrical contact is formed between the tip and a CNT, the current does not show a strong dependence on the contact force. Their study proved that, because of the nanosized contact area, a contact force of 15 nN is already sufficient to establish electrical contact between a Au-coated tip and a SWCNT. Moreover, because of their small diameters when compared to the tip radius of curvature (radius of tube 50 times lower than radius of tip), SWCNTs can easily cut through the thin contamination layer and are in this regard to be compared to sharp knives.¹⁶

C-AFM measurements, using the previously selected PtSi tips, were performed at different contact forces on both the initial SWCNT films as well as on the composite sample (detailed results are presented in the [Supporting Information](#)). On the basis of the results obtained, it was decided that a contact force of 50 nN should be sufficient to obtain reproducible and quantifiable results in terms of current images and measured resistance, respectively, with minimum damage to the samples and the tips.

Selecting the Humidity Levels. Ambient conditions can have a strong influence on nanometer-scale electrical measurements because air contains different contaminants as well as water that always forms a thin layer on the surface of the sample and the tip. Because of this, most C-AFM measurements are done in an inert atmosphere.^{4,10,17} However, in a previous study we have shown that our SWCNT films are highly sensitive to switching from ambient conditions to an inert atmosphere due to the associated CNT dedoping.⁷ Therefore, C-AFM measurement were performed at humidities of 0%, 10% and >50% to determine the humidity effect on the results obtained (detailed results are presented in the [Supporting Information](#)). Results showed that a humidity of $RH \approx 10\%$ lowered the water content sufficiently to ensure acceptable current variations at lower contact forces (that is, ~ 50 nN), but also maintained the required level of doping in the sample that ensures ohmic contact with the tip. Therefore, a humidity of 10% was chosen and maintained throughout all C-AFM measurements. To prevent the remaining water from dissociation leading to oxidation of the tip or the sample, we applied very low bias voltages of -150 to 150 mV during the measurements (the redox potential of pure water is -1.23 V).¹⁸

Quantitative C-AFM on SWCNT Films. These films are the reference conductive network used to determine the network electrical properties without the influence of a polymer matrix. C-AFM has been used before to determine contact resistances between the tip and individual SWCNTs as well as the contact resistance between two tubes or two bundles of tubes.^{17,19} However, when it comes to CNT networks, nonimpregnated or impregnated with a polymer, most studies focus on imaging the conducting paths and not on quantifying their electrical properties.

In general, the total measured resistance can be described by the expression

$$R_t = 2R_C + R_{\text{network}} \quad (2)$$

where $2R_C$ is the total contact resistance between the two electrodes (tip and substrate/wire) and the sample, also called two-terminal contact resistance. As discussed before, the contact resistance varies for different types of metal electrodes as well as for different types of SWCNT. This and the nanosized contact area between a SWCNT and an electrode causes $2R_C$ to vary in a range from several k Ω to several M Ω ,^{9–12} with metallic tubes giving the lowest values. Considering that the sample sheet resistance is $15 \text{ } \Omega/\text{sq}$ and that this value increases only approximately 5–6 times after polymer impregnation, corresponding to a conductivity of $\sim 6 \times 10^3 \text{ S/m}$ (based on results obtained in a previous study)²⁰ it is not likely that this change can be detected via C-AFM, making R_{network} negligible compared to $2R_C$. The apparent contact area between the tip and the sample is orders of magnitude smaller than the apparent contact area between the second electrode and the sample, and therefore $R_{C_{\text{sub-sample}}}$ becomes negligible in comparison to $R_{C_{\text{tip-sample}}}$. The total measured resistance then becomes

$$R_t \approx R_{C_{\text{tip-sample}}} \quad (3)$$

However, each SWCNT is a resistor by itself with an intrinsic resistance of $1\text{--}30 \text{ k}\Omega$,^{21–24} values that are close to the theoretical predictions of $6.5 \text{ k}\Omega$ for ballistic transport.^{21,22} The contact resistances between individual SWCNTs are in the range of tens of k Ω to several M Ω ,^{10,25,26} because of their wide range of possible orientation-dependent structural configurations and different electronic properties from semiconducting to metallic. This means that although C-AFM might not be sensitive enough to determine the large-scale resistance of our sample, the technique can still be used to determine the nano/microscale local electrical properties of the sample.

C-AFM measurements were done on a $2 \text{ } \mu\text{m}$ thick SWCNT film using PtSi-coated tips, at $RH \approx 10\%$ and at a contact force of 50 nN . To prevent tip and sample damage, only point measurements were taken for these SWCNT films and the resistance was calculated based on the slope of the I – V curve. Each I – V curve was repeated two to three times to verify its stability and measurements were taken at 12 different locations on the sample at a distance of $\sim 1 \text{ mm}$ from the Au wire.

Figure 2a, b shows the distribution of the resistances measured on the $2 \text{ } \mu\text{m}$ thick SWCNT films using two fresh PtSi tips. Both distributions are very wide with the larger resistance values over 100 times higher than the smaller ones (the smallest resistances measured were $R_{t \text{ min}} = 340\text{--}420 \text{ k}\Omega$, whereas the largest values measured were $R_{t \text{ max}} = 42\text{--}64 \text{ M}\Omega$). The SWCNT film is basically a network of entangled tubes and ropes of aligned tubes (in a diameter range from one to several tens of nm)²⁰ with holes as deep as 100 nm , and gaps from tens to hundreds of nanometers wide between the tubes (Figure S1a). Considering that the PtSi tips have a curvature radius of approximately 25 nm (Table S1), the differences in the measured resistances are due to a variety of possible contact configurations (example in Figure 2c). Therefore, if the tip is contacting multiple tubes/bundles, the effective contact area is larger, leading to a smaller contact resistance and vice versa.

The real contact area between the tip and the sample cannot be measured due the “porous” nature of the sample and is, therefore, replaced by an apparent contact area. In order to estimate the effect of the apparent contact area on the measured resistance R_t a series of flat Au-coated probes with

Figure 2. (a, b) Distribution of resistance values obtained for two fresh PtSi tips on a 2 μm thick network and (c) schematic describing two examples of different contact configurations with different effective contact areas between the tip and the SWCNT film.

surface areas of 0.45–12 mm^2 (for probe diameters of $d = 0.8$ –4 mm, examples in Figure 1a) were tested. Two identical probes for each diameter were placed on opposite sides of the 2 μm thick SWCNT film (Figure 1b) and the resistance between them was measured. On the basis of these results, an estimate of $R_t = 1.1 \text{ M}\Omega$ was made for an apparent contact area of 1 nm^2 (based on a tube diameter of 1 nm) across the 2 μm thickness of the SWCNT film. However, the distance between the conductive tip and the Au wire used in the C-AFM measurements is $\sim 1 \text{ mm}$. Because the resistance across the network also depends on the distance between the two electrodes, the estimated value of 1.1 $\text{M}\Omega$ for 2 μm would increase further for a distance of 1 mm between the electrodes. Therefore, two probes with a surface contact area of 5 mm^2 were used to determine the resistance variation with the distance between the electrodes, along the surface of the SWCNT film. Using a linear fit to these results (Figure 3b), R_t

Figure 3. Measured resistance R_t for (a) different contact areas and (b) different distances between electrodes measured for an apparent contact area of 5 mm^2 (standard deviation of the population σ_x based on 20 and 15 measurements, respectively, for each data point).

$\approx 6.5 \Omega$ can be calculated for a distance of 2 μm between the probes. This value is very similar to the 4.3 Ω measured across the width of the same SWCNT film (red data point in Figure 3a), implying that, despite possible in-plane orientation due to the preparation procedure,²⁰ the network is still fairly isotropic.

The apparent contact area is always larger than the real contact area and the previous experiments are susceptible to many possible errors related to contact force and probe alignments. Therefore, the R_t calculated based on these experiments is only a rough approximation. However, the estimated value of $R_t = 1.1 \text{ M}\Omega$ partially verifies the results obtained via C-AFM for the same 2 μm thick film (Figure 2a, b), where R_t measured has values around several $\text{M}\Omega$. These

results can be used further to estimate and compare the contact resistance between the SWCNT film and the two electrodes (the tip and the Au substrate/wire).

Quantitative C-AFM on SWCNT Composite. A 2 μm thick SWCNT film was impregnated with an epoxy/amine polymer (referred to as composite sample) and embedded in a polymer matrix for microtoming. C-AFM measurements were done directly at the cross-section of the bulk sample or on cut sections of different thicknesses.

Bulk Composite Sample. The distinction between the composite areas and the pure polymer area is very clear in topography images as well as in phase images, where the cut CNTs sticking out at the surface of the composite give a different roughness and phase contrast as compared to the embedding polymer (Figure 4).

Figure 4. Composite film $\sim 2 \mu\text{m}$ thick, embedded in a polymer matrix: (a) topography and (b) phase contrast images. (Note: These images contain tip related artifacts and are shown merely as an example of the typical topography/phase contrast images obtained using the standard AFM technique.) Complementary SEM images are shown in Figure S6a, b.

All C-AFM measurements were done under the same conditions ($\text{RH} \approx 10\%$, contact force of 50 nN) as the previous measurements. Because the composite sample has a higher mechanical stability than the SWCNT films, current images were also taken in addition to I – V curves. The ohmic contact between the tip and the sample and a constant contact force ensure that reliable resistance values are obtained using Ohm's law $R = V/I$ from images as well as from the slope of the I – V curves for point measurements.

Figure 5a shows a clear separation between the composite and the embedding polymer with no current gradient toward the edges, suggesting that the CNTs do not detach from the main film during the polymer impregnation process to diffuse into the polymer. The homogeneous distribution of conductive areas in the composite at a microscale as well as at a nanoscale (Figure 5b, c) also suggests a uniform polymer impregnation throughout the whole width of the CNT film.

Current maps of individual clusters show that they can have sizes from several nm to several tens of nm (Figure 5d–g). This range coincides with the diameter range of the CNT ropes in the initial film, confirming the presence of SWCNT ropes in the composite film as well. The resistance of these clusters/ropes shows a range of values irrespective of their size. This variation can be explained by the different contact configurations that the measured rope can have with the rest of the CNT network inside the composite. All current maps show a high resistance edge of several $\text{M}\Omega$ around the measured clusters. However, these maps are subjected to a default smoothening process. By comparing the smoothed images with the pixelated ones (example in Figure 5g, and h), we verified

Figure 5. Current images of (a–c) composite film at different magnifications, (d–f) individual SWCNT clusters of different current/resistance values, (g, h) comparison between smoothed and pixelated image of a 10 nm cluster with (i) resistance profile across 10 nm cluster, and (j) a schematic illustrating the transition from conductive areas to insulating areas and its effect on the measured current values.

that the high-resistance edges are not an artifact, and that these edges actually confirm the transition from conductive areas to insulating areas, as schematically shown in Figure 5j. Therefore, the current maps can be used to calculate the resistance in different points on the sample (example in Figure 5i).

The I – V curves taken randomly on the composite film showed the same type of resistance distribution as those calculated based on the current images (Figure 6), proving that the current images taken can be quantified in a reliable way. In order to verify the sample homogeneity in the depth as well as at the surface, a microtome was used to cut away thin sections from the composite, and the same measurements were repeated after removing at least $2\ \mu\text{m}$ of material from the surface of the sample. The same range of values for the measured resistance

Figure 6. Resistance distributions calculated based on (a) current images taken at the two cross-cuts and (b) point measurements (I – V curves).

was obtained in both cases, implying composite homogeneity at the surface as well as in the bulk.

The network resistance R_{network} for the composite sample is as high as $75\ \Omega$ (≈ 5 times higher than the nonimpregnated SWCNT network) and is negligible compared to $R_{\text{C, tip-sample}}$, which is in the range of tens of $\text{k}\Omega$ to several $\text{M}\Omega$ (details in section Quantitative C-AFM on SWCNT Films). This means that the total resistance measured is determined by the contact resistance between the tip and the sample and the contact resistance between the measured SWCNT cluster/rope and the rest of the network. A schematic of the tip–sample contact configuration and its equivalent electrical circuitry for the initial SWCNT film and the composite sample is given in Figure S7.

Because the polymer filled the gaps between the tubes, the tip is only in contact with the surface of the composite sample (Figure 7b), contrary to the SWCNT films, where it could

Figure 7. Schematic of contact configurations between the tip and the sample for (a) SWCNT films and (b) cross-section of composite film.

penetrate deep into the network (Figure 2c). Even if the surface of the composite at the cross-section is rough, the tip can only be in direct contact with the CNTs sticking out of the polymer. In addition, the curvature radius of the tip is similar to or even larger than the diameter of the SWCNT ropes. Consequently, the contact area variation between the tip and the composite sample is negligible as compared to the SWCNT films and therefore should not lead to large resistance variations on its own. Therefore, the wide range of resistance values is also explained by the composite nature of the sample where the insulating polymer can significantly increase the local measured resistance. However, the initial SWCNT films gave a similarly wide range of resistances. This can only be explained by the different contact configurations between the tip and the two types of sample (Figure 7).

The tip is placed at the surface of the SWCNT film, with the contact taking place at the sides of the tubes/bundles, and at the cross section of the composite film, with contact taking place at the end part of the tubes/bundles (Figure 7, magnified boxes). This configuration has a double effect on the measured resistance. First of all, the contact area is larger at the end part of the tubes/bundles, where the large tip can be in direct contact with multiple tubes and the effective contact area can be as large as the bundle diameter. When the tip is touching the side of a bundle, it can only be in direct contact with the tube(s) at the exterior of the bundle, resulting in a small contact area as compared to the bundle diameter. Second, when the tip is contacting only the edge tube(s) of the bundle, additional tube–tube contact resistances are required to ensure the electrical transport from one tube within the bundle to another. These additional resistances are not required if the tip is directly in contact with most/all of them. Therefore, the resistances measured for the SWCNT films are not really

comparable to the resistances measured for the composite films because of different tip–sample contact configurations.

Thin Composite Sections. Using an ultramicrotome, sections with the thickness in the range of 150–350 nm were cut from the composite sample and deposited on Au-coated substrates (Figure 8a). The thickness of the sections was

Figure 8. (a) Example of thin sections of SWCNT composite embedded in a polymer with (b) height profile across a section, (c) current image, and (d, e) resistance distributions for sections of 350 and 150 nm thickness, respectively. Complementary TEM images are shown in Figure S6c, d.

verified via height profiles taken by AFM at the edges of the sections (Figure 8b, height profile taken across black dotted line in Figure 8c). C-AFM measurement were done on these sections in the same manner as at the cross-section of the bulk sample. The contrast between the Au substrate, the composite film, and the pure polymer is very clear in terms of current distribution (Figure 8c).

Similar results were obtained for both the bulk sample as well as the cut sections in terms of composite homogeneity. The measured resistance values also varied from ~ 100 k Ω up to >10 M Ω for all sections. However, the distribution of these values is different. The resistance distributions for the bulk composite sample showed a peak at $R_t < 1$ M Ω (Figure 6), whereas composite sections show a peak at $R_t = 2$ –5 M Ω (Figure 8d, e). This difference is directly related to the thickness of the composite contained between the two electrodes and the SWCNT network comprised within.

The distance between the electrodes when measuring the bulk composite sample is >5 mm. In this case, the total measured resistance is described by expression (2): $R_t = 2R_C + R_{\text{network}}$. The value of R_{network} , which is as high as 75 Ω , is negligible compared to $2R_C$ which is in the range of tens of k Ω to several M Ω . Since the apparent contact area between the tip and the sample is orders of magnitude smaller than the apparent contact area between the second electrode and the sample, $R_{C_{\text{sub-sample}}}$ becomes negligible in comparison to $R_{C_{\text{tip-sample}}}$. The total measured resistance is therefore also described by expression (3): $R_t \approx R_{C_{\text{tip-sample}}}$.

When measuring thin sections, the distance between the two electrodes is equal to the thickness of the section of about 150–350 nm, a value much smaller than 5 mm for the bulk composite. This should reduce R_{network} even further with expression (3) describing the total resistance for both the sections and the bulk composite sample.

In a previous study, we designed a simple model to describe the conductive network within this composite.⁷ A Unit Block (UB) was defined as a SWCNT network comprised of a block with $2 \times 2 \times t \mu\text{m}^3$, where $2 \mu\text{m}$ is the average full length of a tube and t the thickness of the SWCNT film (with 2.5×10^3 UBs fitting between two electrodes at a distance of 5 mm). This UB acts as the smallest possible network that can be formed without cutting the full length of the tubes. Because the length of the SWCNTs and the high network density make it almost impossible for a tube to have only one single connection, directly or indirectly, with another tube, all tubes within a UB are considered to be connected in parallel. Shortening the tubes reduces their possibility to form multiple contacts with other tubes, and therefore, upon cutting the tubes by sectioning, series connections become more likely than parallel ones.

In the real sample, there is no such clear/simple network arrangement within one UB, but the length of the tubes is still the largest factor that influences the ability of a tube to form parallel connections. Considering that the SWCNT network has holes of hundreds of nanometers wide between different bundles (Figure S1a), it is most likely that the tubes within our thin sections do not have sufficient length/space to be representative for the overall SWCNT network. To be more precise, the sections are too thin to contain a typical part of a SWCNT network, with a proper representation of both parallel and series connections, and in a section the tubes are more likely to have series connections or no connections at all with other tubes. In this case, the total resistance is actually described by

$$R_t = R_{C_{\text{tip-sample}}} + nR_{\text{intrinsic}} + mR_{C_{\text{tube-tube}}} \quad (4)$$

where n and m represent the number of tubes and tube–tube junctions, respectively, that form the conductive path between the tip and the second electrode.

The contact resistance $R_{C_{\text{tip-sample}}}$ is roughly the same for sections and the bulk composite while the intrinsic resistance of the tubes is about 1–30 k Ω . This means that the resistance peaks at 2–5 M Ω for the composite (Figure 8d, e) are actually dominated by the contact resistances between the tubes forming the conductive paths. Because of the large variety in SWCNT electronic properties, contact resistances between individual tubes/bundles of tubes have been reported in a range of values from tens of k Ω to several M Ω .^{10,25,26} The polymer impregnation process, to which the initial SWCNT network was subjected, also created tunneling between the tubes/bundles by pushing them apart or even by introducing polymer between contacting tubes. The latter especially leads to very high contact resistances.^{27–29} Because of the large range of values these tube–tube contact resistances can have, it is difficult to estimate how many junctions a conductive path contains on average. However, since resistance values as low as 100 k Ω have been measured for the thin sections as well, a value which is roughly the same as $R_{C_{\text{tip-sample}}}$ (eq 3), we can conclude that there are also direct conductive paths created by individual tubes or bundles of tubes contacting both electrodes (tip and substrate).

CONCLUSIONS

Quantitative C-AFM is not (yet) a very common technique due to many difficulties encountered, from tip material wear and compatibility with the sample to environmental conditions and contact force used during measurements. In addition, the complexity of the contact configurations between the tip and

the sample, the real contact areas and even the distance between the electrodes make it very difficult to compare results from different studies done on similar materials. Moreover, the technique still has significant limitations when low resistance samples are considered. Electrical characterization of materials at the nanoscale can only be achieved with very small contact areas between the tip and the sample, which in turn comes with the drawback of a high contact resistance between the two. Although the conductive tips are continuously improved with lower curvature radius, higher conductivities, and improved hardness, the technique is still not able to quantitatively measure samples with resistances below several k Ω .

We have established the suitable tools and conditions needed for reproducible and quantitative C-AFM measurements that can be done on SWCNT films and composite samples and studied the influence of different tip-sample contact configurations on the measured resistance. Point measurements were combined with scans and resistance values calculated via *I*-*V* curves were used to verify the reliability of the resistance values obtained via current images to ensure quantitative current maps of the sample.

The high conductivity of the samples makes it impossible to measure the macroscale resistances of our conductive networks (either as a film or as a composite) using only C-AFM, as the tip-sample contact resistance is often dominating. By cutting thin sections of 150–350 nm from the composite, we increased the sample resistance and managed to separate the tip-sample contact resistance from the sample resistance. However, describing a SWCNT network as a mixture of series and parallel connections, quantitative C-AFM on these thin sections showed that they are not representative for the typical, isotropic network. Despite this, the technique was successfully used to identify and characterize local electrical properties of a SWCNT composite material, such as sample homogeneity, resistance range of individual clusters, and their electrical characteristics.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06201.

Measurements performed in order to determine the suitable conductive AFM tips, contact force, and humidity levels and the results obtained, additional SEM and TEM images of the bulk composite and composite sections, respectively, equivalent electrical circuitry for different tip-sample contact configurations (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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