

Spontaneous Charging of Single-Walled Carbon Nanotubes: A Novel Strategy for the Selective Substrate Deposition of Individual Tubes at Ambient Temperature

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A spontaneous gas-phase charging phenomenon of single-walled carbon nanotube (CNT) bundles synthesized with an aerosol (floating catalyst) method has been discovered. CNT bundles were naturally both positively and negatively charged with up to four elementary charges, whereas individual nanotubes remained electrically neutral. On the basis of the observed self-charging of CNTs, a novel method for the gas-phase separation of individual CNTs from bundles and their subsequent deposition on any substrate at ambient temperature was developed.

Introduction

Individual single-walled carbon nanotubes (CNTs) are promising building blocks for nanoscale devices due to their small size and unique nearly one-dimensional structure. CNT-based architectures such as field-effect transistors,¹ memory devices,² quantum wires,³ and logic gate circuits⁴ already have been demonstrated. To fully utilize CNTs in these applications, methods for placing individual CNTs with controlled purity, length, and chirality onto selected locations on substrates at ambient temperature need to be investigated. Accordingly, the development of straightforward methods for the controllable synthesis of individual CNTs is extremely desirable. However, this is still a challenging task since CNTs tend to spontaneously bundle, and as a result, most of the CNT synthesis methods produce thoroughly bundled tubes.^{5–8}

To exfoliate the bundles, an additional step, CNT functionalization, based on the use of, for instance, different types of chemicals as surfactants,⁹ polymers,¹⁰ peptides,¹¹ etc. is typically required. However, the functionalization can significantly alter the original properties of the CNTs.¹² Additionally, when individual tubes are deposited from a solution to a substrate, CNTs may re-bundle during solvent evaporation. Moreover, CNTs usually need to be purified from byproducts (inactive metal particles, catalyst support, amorphous carbon, etc.) prior to their utilization. For the direct synthesis of isolated CNTs, supported chemical vapor deposition (CVD) methods have been applied.^{13–17} However, high growth temperatures (between 400 and 1000 °C) requirements inevitably limit the utilization of temperature-sensitive substrate materials and prohibit simple integration of the CNTs into many nanoscale electronic devices.

Recently, we developed a novel floating catalyst (aerosol) CVD process, the so-called hot wire generator (HWG) method, for the selective production of single-walled¹⁸ or

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multiwalled¹⁹ CNTs. This method relies on the introduction of size-controlled pre-made catalyst particles,²⁰ synthesized via physical vapor deposition (PVD) using a hot wire particle generator, into conditions favorable for CNT formation. Key characteristics of this approach are the high efficiency of catalyst particle utilization for CNT formation, high purity of the produced CNTs, and excellent controllability of the number concentration of catalyst particles, and consequently, nanotubes in the gas phase.^{16,19,21} Accordingly, the latter gives possibility to control the CNT bundling process.

In this article, we present a novel, continuous process for the gas-phase CVD synthesis, in situ separation, and deposition of individual single-walled CNTs on a wide variety of substrates at ambient temperature. This approach is based on our discovery of the spontaneous charging of CNTs in the gas phase due to their bundling. The gas-phase CNT number concentration was controlled by varying either number concentrations of catalyst clusters or amount of carbon source, CO, available for the CNT formation. The charged CNTs (bundles) are removed from the gas by applying an electric field in an electrostatic filter (ESF). The remaining noncharged fraction of individual CNTs is deposited at ambient temperature by thermophoresis. Alternatively, noncharged CNTs can be electrophoretically deposited after their charging in a corona charger (Supporting Information).

In the following, we first describe studies to determine the charging of bundled CNTs and the electrical neutrality of individual CNTs in the gas phase at the reactor outlet. We experimentally show that the charged CNT bundles can be selectively separated from the gas by applying an electric field. Also, we demonstrate the selective deposition of individual CNTs at ambient temperature onto various substrates, including thin carbon film on copper electron microscopy grids, oxidized silicon wafers, Si₃N₄, and thick polymer films.

Experimental Section

The HWG reactor for the growth of CNTs has been described in detail elsewhere (Supporting Information).¹⁸ Unless otherwise stated, all the experiments were carried out by heating the wire with 19.0 W power, a CO concentration of 53% in a CO and Ar/H₂ (93/7) mixture, and a reactor temperature of 700 °C. The experimental setup includes a CNT synthesis reactor, an integrated ESF for removing charged CNTs from the reactor outlet gas, a differential mobility analyzer (DMA) system, and a thermophoretic or electrostatic collector for depositing CNTs onto a substrate. The DMA is a standard tool in the field of aerosol science for determining particle number size distributions in the gas phase.²² The DMA system consists of a classifier, a condensation particle counter, and a ²⁴¹Am bipolar charger (optional). The classifier

contains two electrodes between which charged aerosol particles are classified according to their electrical mobility (*Z*), which, in turn, depends on both the particle size and their electrical charge. This method allowed us to unambiguously distinguish the conditions of CNT formation, without having to resort to time-consuming transmission electron microscopy (TEM) observations.²³ For instance, CNTs produced by the HWG method were detected at mobility diameters higher than 10 nm, while catalyst particles were observed at mobility diameters below 10 nm.²³ Adequate power supplies for applying both positive and negative polarity to the classifier internal electrode were used, while the external electrode was kept grounded. The ESF was located downstream of the reactor and was used to filter out the charged CNTs when required. For structural characterization, TEM imaging of the CNTs collected on carbon-coated copper grids was carried out.

Results and Discussion

The mobility size distribution of the naturally charged CNTs and nonactive catalyst particles (i.e., obtained without the ²⁴¹Am bipolar charger prior to the DMA) is illustrated in Figure 1a. The figure shows the dependence of the measured frequency on both the equivalent mobility diameter, *D*, and the inverse electrical mobility, 1/*Z*. *D* was calculated assuming a spherical shape and a single charge of aerosol particles on the basis of the Millikan equation.²⁴ As can be seen, a broad mobility distribution with a mean mobility diameter of around 45 nm was obtained regardless of the polarity of the DMA bias voltage and was attributed to the presence of CNTs. TEM observations showed that the CNTs were single-walled and clearly aggregated in bundles (Figure 1b). Since the DMA can classify only charged aerosol particles, mobility distributions indicate that the nanotubes coming from the reactor were naturally charged. Similar results for the CNT number concentration downstream the reactor were obtained by direct measurements using the condensation particle counter with and without applying a potential difference in the ESF prior to the counter. Furthermore, the charging phenomenon was observed independently of the polarity applied to the DMA classifier. According to the measurements, the CNTs were approximately equally positively and negatively charged with fractions of 47 and 53%, respectively (Table 1).

To study the charge state of the produced bundles, tandem DMA measurements were carried out. For this purpose, a first DMA was used to extract naturally positively charged 40 nm mobility selected tubes, which were then introduced through the ⁸⁵Kr neutralizer into a second DMA. The results of the second DMA mobility measurements revealed that the CNTs can carry up to four elementary charges as shown in Figure 1c. This was found on the basis of an analysis of the DMA distributions by means of Gaussian fitting taking into account the change in the charging state of the CNTs in the neutralizer.

Since the synthesis of CNTs relies on the introduction of the pre-made catalyst particles, which, in turn, might possess electrical charges after their formation, the CNT charging

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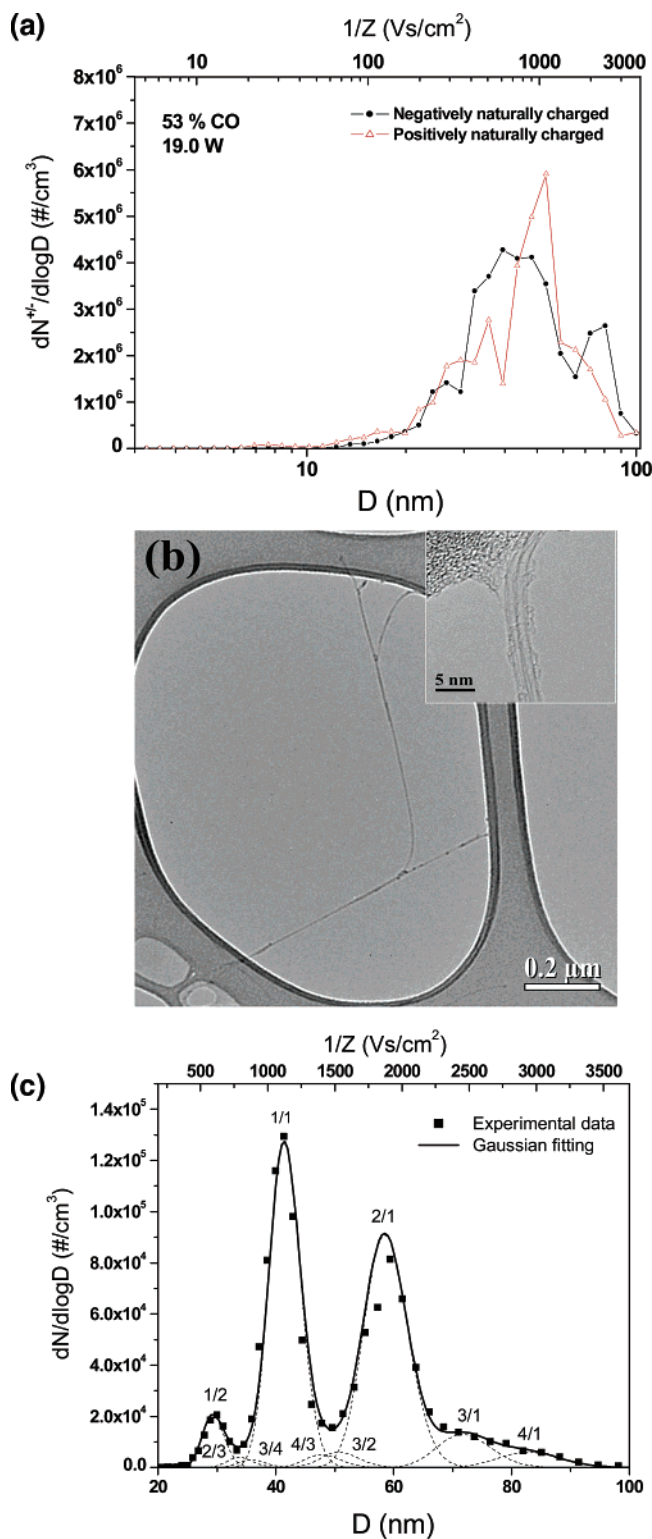


Figure 1. (a) Mobility size distribution of positively and negatively naturally charged fractions of CNTs in the gas phase as measured using DMA without ²⁴¹Am bipolar charger. (b) TEM image of the as-grown CNT bundles. (c) Results of tandem mobility measurements of naturally charged 40 nm mobility selected CNTs demonstrating the charge state of the produced CNTs (charging state of the CNTs are represented as follows: original number of charges/number of charges after passing through the neutralizer).

can be conjectured to originate from the particles. Indeed, literature data on metal nanoparticle formation in different HWG systems^{25,26} have indicated the presence of charged particles. To examine the charge state of Fe catalyst particles

Table 1. Fraction of Charged CNTs ($N^{+/-}/N$, Where $N^{+/-} = N^+ + N^-$; N^+ and N^- Are the Number Concentration of Positively and Negatively Charged CNTs, Respectively) of the Total CNT Number Concentration (N), Synthesized Using 53% CO and a Heating Power of 19.0 W, at Different Reactor Temperatures

temperature (°C)	$N^{+/-}/N$ (%)	$N^+/(N^+ + N^-)$ (%)	$N^-/(N^+ + N^-)$ (%)
700	99	47	53
800	99	48	52
900	97	41	59

Table 2. Fraction of Charged Fe Catalyst Particles ($N_p^{+/-}/N_p$, Where $N_p^{+/-} = N_p^+ + N_p^-$; N_p^+ and N_p^- Are the Number Concentration of Positively and Negatively Charged Particles, Respectively) of the Total Particle Number Concentration (N_p)

temperature (°C)	$N_p^{+/-}/N_p$ (%)	$N_p^+/(N_p^+ + N_p^-)$ (%)	$N_p^-/(N_p^+ + N_p^-)$ (%)
25	1	99	1
700	1	4	96
800	4	27	73
900	2	28	72

in our system, CO was replaced by N₂ to prevent the formation of CNTs in the reactor. Experiments at temperatures from 25 to 900 °C showed that practically all catalyst particles (up to 99%) were electrically neutral (Table 2), suggesting a different mechanism of the CNT charging rather than from the catalyst particles.

In an attempt to measure the mobility size distributions of the neutral aerosol particles, the reactor outlet gas was passed through the ESF to filter out the charged objects by applying a potential difference between electrodes. Then, the neutral aerosol particles were artificially charged using the external bipolar charger (²⁴¹Am) prior to the mobility distribution measurements. After converting mobility size distributions to number size distributions assuming equilibrium charge distribution, we observed only a single peak with a mean mobility equivalent diameter of 5 nm, assigned to catalyst particles inactive for the CNT growth as confirmed by TEM analysis, with 2 orders of magnitude lower concentration compared to that of the naturally charged CNTs (Figure 1a). Thus, all the CNTs were deposited in the ESF and, hence, were electrically charged. Similar results were obtained at reactor temperatures of 800 and 900 °C (Table 1).

It is known that gas surface reactions may induce electronic excitations at metal surfaces. When highly exothermic reactions take place, these excitations may lead to the ejections of ions and electrons from the surface.²⁷ Consequently, it can be speculated that the exothermic CO disproportionation and hydrogenation reactions²¹ providing carbon atoms for the CNT growth might be responsible for the electrical charging. In an attempt to examine this hypothesis, experiments were carried out varying the CO concentration. This also allowed us to control the fraction of active catalyst particles initiating the CNT growth and, subsequently, the CNT concentration and their bundling probability. To quantitatively estimate the fraction of charged CNTs, mobility size distributions were measured with the ²⁴¹Am bipolar charger. Figure 2a shows the comparison

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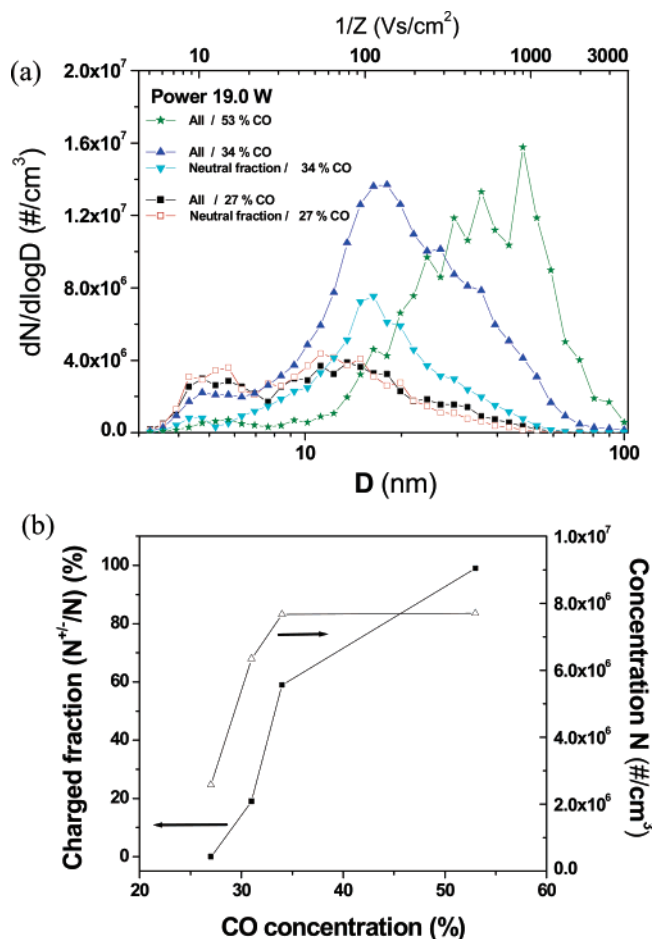


Figure 2. (a) Comparison between the number size distributions of all and neutral CNTs and catalyst particles at different CO concentrations, using a heating power of 19 W, measured using DMA with ²⁴¹Am bipolar charger. When CO concentration is 53%, all of the CNTs are naturally charged. (b) Charged fraction of CNTs ($N^{+/-}/N$) and number concentration (N) plotted versus the CO concentration.

between the mobility size distributions of all (ESF off) and neutral (ESF on) CNTs at CO concentrations of 27, 34, and 53%. As is expected, the CNT concentration increased with the concentration of the carbon source introduced into the reactor. At the CO concentration of 27%, the mobility size distribution of all CNTs and nanotubes after filtering out the charged fraction appeared to be identical, indicating that almost all the tubes were electrically neutral. However, the fraction of neutral CNTs gradually decreased as the CO concentration was increased. Therefore, at 53% of CO, almost all the CNTs were charged. Figure 2b illustrates the effect of the CO concentration on the total fraction of charged nanotubes and on the total concentration of CNTs. These results show that the higher CO concentration leads to the higher charging of CNTs. However, the question of which process, either the exothermic reactions or bundling of CNTs, is responsible for the charging is still open.

To clarify this point, additional experiments were carried out by varying the heating power applied to the wire from 16.0 to 19.0 W at the highest CO concentration of 53% (Figure 3a). This allowed us to vary the concentration and thus bundling of CNTs, without changing the charging contribution due to the exothermic reactions. As can be seen in Figure 3a,b, the fraction of the charged CNTs increased

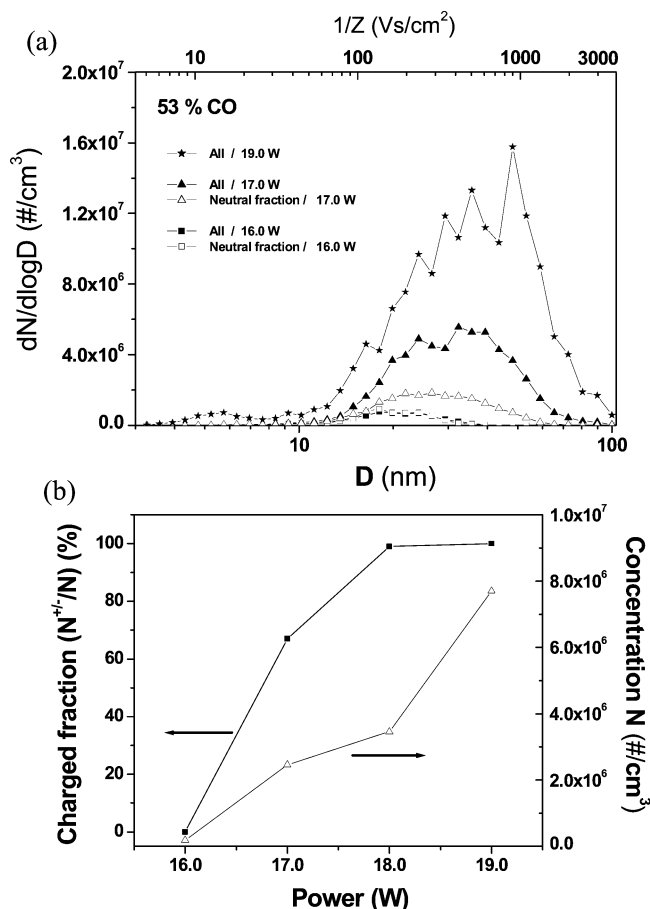


Figure 3. (a) Comparison between the number size distributions of all and neutral CNTs at different hot wire heating powers when CO concentration is 53% measured using DMA with ²⁴¹Am bipolar charger. When heating power is 19.0 W, all of the CNTs are naturally charged. (b) Charged fraction of CNTs ($N^{+/-}/N$) and number concentration (N) plotted versus the hot wire heating power.

with the power applied to the heated wire, ruling out the exothermic reactions as the origin of the CNTs charging.

The experimental results showed that a higher concentration of CNTs led to a more effective charging. This fact is believed to be related to the bundling of the CNTs since the probability for bundling increases with their concentration in gas phase. Accordingly, the natural charging of the CNTs may occur due to the formation of bundles in the gas phase. This hypothesis was supported by TEM observation of the sample containing charged CNTs, where only bundled CNTs were found (Figure 1b). To further examine this hypothesis, CNTs were synthesized using a heating power of 16.5 W to maintain a small concentration of CNTs and, thereby, to reduce their bundling. At these experimental conditions the fraction of charged CNTs estimated from Figure 3b was around 30%. CNTs were collected from the gas phase onto a TEM holey carbon film substrate using a point-to-plate electrostatic precipitator (Supporting Information). TEM observations of the product collected after the reactor revealed the presence of both bundles and individual CNTs (Figure 4b). However, the product collection downstream of the operating ESF showed the presence of individual CNTs (Figure 4a). This indicates that individual CNTs were electrically neutral whereas bundled CNTs were charged.

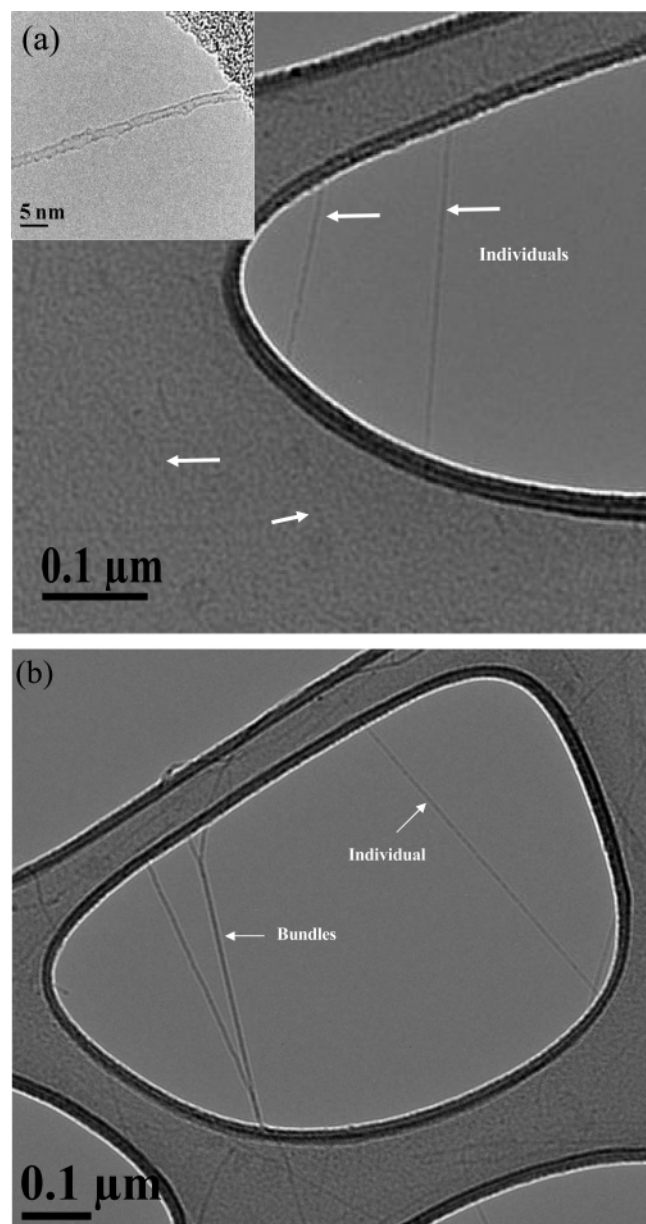


Figure 4. TEM images of (a) individual CNTs collected after filtering charged bundles with ESF and (b) both individual and bundles of CNTs collected without ESF filtering.

To statistically confirm these results, we carried out careful TEM investigations. It was found that neutral CNTs consisted of 94% individual CNTs, and the sample with 99% naturally charged CNTs contained 93% bundled CNTs. In both cases the statistic sample involved 70 counts. The presence of a small fraction of charged individual CNTs can be explained due to the thermal ion emission or collisions of neutral tubes with ions available in the gas phase. Conversely, the presence of a small fraction of neutral bundled CNTs can be related to possible CNT bundle discharge processes.

The experimental results showed the presence of multiply charged CNTs, suggesting that some highly energetic process occurs during the bundling. We propose that this process is related to the van der Waals energy release. To minimize their free energy, CNTs form bundles consisting of tubes located parallel to each other. This results in a relatively high energy release: for example, the bundling of two armchair (10,10) CNTs leads to an energy decrease of as

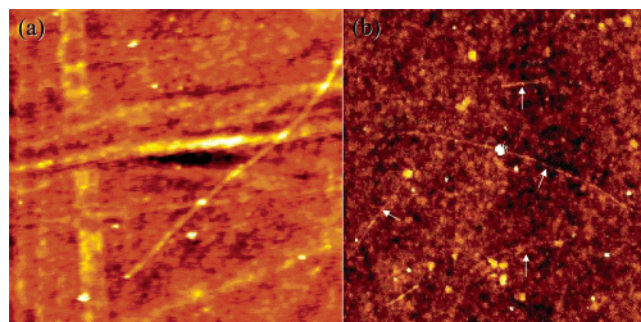


Figure 5. AFM images of individual CNTs deposited onto (a) a temperature-sensitive epoxy-based substrate (SU-8; 10 μm thick layer) and (b) a Si₃N₄ substrate (119 μm thick layer).

much as 95 eV/100 nm compared to two isolated tubes.²⁸ This energy can be released due to the thermal dissipation and emission of ions from the surface of the formed bundle. The latter is believed to result in the observed charging phenomenon.

Most of the individual CNTs were found to be electrically neutral. This allows us to present a novel strategy for the separation of individual and bundles of CNTs synthesized in the gas phase. Since the sample collection was carried out at ambient temperature, this approach enables us to deposit individual CNTs on a wide variety of substrates, including also those substrate materials which cannot withstand elevated temperatures. As an example, we used an epoxy-based substrate (SU-8, 10 μm thick layer), with a degradation temperature of ~300 °C, and a Si₃N₄ substrate (119 μm thick layer). The deposition was carried out using the electrostatic precipitator. Atomic force microscopy (AFM) images illustrated in Figure 5a,b showed the presence of individual CNTs with diameters ranging from 0.7 to 1.1 nm as determined from the height measurements. These results were consistent with TEM analysis. In addition, AFM images of individual CNTs collected onto oxidized silicon substrates (260 nm thick layer) and Si₃N₄ substrates (100 nm thick) are shown in the Supporting Information. In the case of the oxidized silicon substrates, the CNT deposition was carried out using a thermophoretic precipitator.²⁹

Conclusion

In summary, the spontaneous charging of single-walled carbon nanotubes synthesized using an aerosol (floating catalyst) method was observed. The origin of this surprising phenomenon was directly linked to the bundling of the nanotubes. Furthermore, on the basis of the charging phenomena, a novel strategy to separate bundled and individual single-walled CNTs, synthesized using the HWG method, and to collect the individuals onto any type of solid substrate, including low-temperature ones, was developed. This method opens new avenues for the direct integration of individual CNTs into molecular electronics based on both

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conventional oxidized silicon substrates and temperature-sensitive materials, e.g., for flexible electronics.

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Supporting Information Available: (i) Description of the experimental setup for the charging studies of CNTs; (ii) AFM topographic images of individual single-walled CNTs deposited on oxidized silicon and Si₃N₄ substrates; (iii) description of the sample collectors used for the CNT deposition at ambient temperature: thermophoretic and electrostatic precipitators. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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