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Inherent carbonaceous impurities on arc-discharge multiwalled carbon nanotubes and their implications for nanoscale interfaces



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ABSTRACT

This paper presents evidence that strongly adhered carbonaceous surface impurities, intrinsic impurities that accompany multiwall carbon nanotubes (MWCNTs) synthesized by arc-discharge, are a component that cannot be ignored in experiments involving single nanotubes and their interfaces with a second surface. At the interface that forms between a carbon nanotube and a graphitic surface, these impurities can significantly alter the adhesion properties of the underlying nanotube and can cause over 30% scatter in computed interaction energies, similar in magnitude to the scatter reported in experimental measurements involving individual CNTs. Also presented is high-resolution TEM evidence that commonly used purification techniques that are effective at removing larger impurity particles from as-produced arc-discharge MWCNT samples do not remove these strongly adhered carbonaceous surface impurities.

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1. Introduction

Carbon nanotubes (CNTs) have been widely investigated for their exceptional electronic and mechanical properties [1–4], which contribute to their effectiveness in high-performance nanocomposites [5,6]. While CNTs are commonly represented and computationally modeled as perfectly ordered concentric shells of carbon, their surfaces often have a thin film of randomly distributed, strongly adhered carbonaceous impurities (Fig. 1). These surface impurities can significantly alter the interactions of the underlying CNTs with their environments, hindering their efficacy in applications and preventing an accurate evaluation of their fundamental properties.

Despite their ubiquitous presence on nanotubes, these carbonaceous impurities are rarely mentioned in the vast CNT literature; the few studies that discussed them only invoked their presence as possible causes for variation in measured properties [7–15]. Surprisingly, most studies of nanotube purification methods—which rely on scanning electron microscopy (SEM), Raman spectroscopy, and low-resolution

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Fig. 1 – Two typical high-resolution transmission electron microscopy (HR-TEM) images of arc-discharge-produced MWCNTs (a and c) and the same images with adhered impurities highlighted in green (b and d). These MWCNTs are referred to as "Structure I" (for a and b) and "Structure II" (for c and d) as discussed in Section 2.1.1. Clusters of impurities that we defined in our computational model to be on the anterior side are filled with green color, and outlined are those defined to be on the posterior side of the tube (see details in Section 2.1.1). (A color version of this figure can be viewed online.)

transmission electron microscopy images for purity analysis—do not characterize the purified materials at sufficiently high resolution to determine if these fewnanometer-thick, strongly-adhered carbonaceous impurities have been removed from the CNT surfaces. Indeed, we have found that these carbonaceous impurities are detectable only through high-resolution transmission electron microscopy (HR-TEM). Though we observed small regions of completely clean CNT surfaces at 5–10 nm length scales, as shown in previous reports [5,16,17], the adhered impurities were consistently present at the longer length scales where nanotubes are measured or employed in applications.

Given our recent interests in evaluating the mechanical properties of CNTs at the nanoscale [15], we suspect that the effects from these impurities may become quite pronounced in experiments involving single nanotubes and their interfaces. In such cases, variations among the surfaces of different nanotubes or among areas on the surface of a single nanotube can significantly affect the nanoscale properties compared to an ensemble of many nanotubes, where average properties are expected. Since the presence, position, and coverage of these adhered impurities are unpredictable, we additionally hypothesize that they are observed primarily as increased scatter in measured properties. Indeed, the large variations found in mechanical measurements involving individual CNTs reported in the literature [14,18,19] can be explained by the presence of adhered carbonaceous impurities. For example, the stiffness of individual multi-walled carbon nanotubes (MWCNTs), measured through their thermal vibrations, varies from 0.4 to 4 TPa [20], which may have partially resulted from varying concentrations of carbonaceous coating on the CNT surfaces. Peeling experiments that study the adhesive interactions between nanotubes and other surfaces also show large scatter [14,15]—with the standard deviation in both experimental surface energy and adhesion force exceeding 40% between different tubes, far beyond the intrinsic experimental error of the measurement technique-that can be easily explained by carbonaceous impurities present at the surface. Further evidence is found in studies of MWCNT rolling or sliding on surfaces [19,21,22], where the lateral force required to induce rolling shows periodicity equal to the MWCNT circumference and can be correlated to the topographical mapping of adhered impurities on the MWCNT surface. These force peaks do not have the regularity that would be expected had they been caused by the atomic corrugation of the graphitic plane [23], and thus are more likely caused by the presence of amorphous carbonaceous clusters over which the tube must roll. A similar force profile was observed when a single nanotube was placed on and peeled from a surface, where peaks and dips far beyond experimental noise were observed in the force measurement [24]. That these large fluctuations were reproduced at the same location along the tube during both approach and retraction are signatures of impurities located on the nanotube's surface.

Additional support for our hypothesis can be found in the much lower scatter in data in studies using carbonaceousimpurity-free graphitic surfaces or those where all measurements were performed using the same surface of a single nanotube. For instance, the experimental interlayer binding energy of graphite was measured with a standard deviation of \sim 5% [25], much less than the variations observed in the aforementioned studies with CNTs [14,15]. While some of this improved consistency can be attributed to a more precise experimental method and the larger size of the graphite surface, which made the system behave more like an ensemble than a single nanotube, it is worth emphasizing that this reduced-scatter trend also holds for experiments conducted repeatedly with individual CNTs. In peeling experiments where the same surface of a single nanotube was peeled multiple times away from a graphitic substrate, little scatter was found in adhesion energy, with standard deviations of ~7-20% [13,14,26].

The aforementioned observations prompted us to undertake a computational evaluation of the variations in interaction strength between a CNT and a graphitic surface in the presence of a carbonaceous coating. Using HR-TEM imaging, we also evaluated the ability of several commonly reported chemical purification techniques to remove carbonaceous impurities from the outer surfaces of arc-discharge-produced MWCNTs. Our findings suggest that the adhered carbonaceous impurities, which are too chemically similar to the MWCNT itself to be selectively removed via chemical strategies, can account for nearly all the scatter in adhesion measurements that have been reported in the literature.

2. Computational and experimental methodology

2.1. Modeling and computation

2.1.1. Measuring dimensions and coverage of adhered impurities

Representative HR-TEM images (Fig. 1) of MWCNTs with identifiable adhered impurities were used to estimate the dimensions of the carbonaceous impurities in an experimental sample. These impurities can be identified by their amorphous appearance in contrast to the crystalline MWCNT walls that appear as straight lines in the electron micrographs. These impurities' shapes and dimensions were then used to develop a computational model with size down-scaling (~10-fold reduction in the number of atoms), as atomistically simulating the entire MWCNT is computationally very expensive (see detailed description in Supplementary Information (SI), Section S1). To identify the effects of differing shapes and loadings of impurities, we selected two model nanotubes with widely different surface coverage: one where there is a small amount of impurity located at a single location on the side of the nanotube ("Structure I," Fig. 1b), and one where there are more impurities, which are distributed over the entire surface ("Structure II," Fig. 1d). Since we could not determine whether the impurities lie above or below the MWCNT in the HR-TEM image (Fig. 1d), we simply defined their location in our model.

2.1.2. Energy profile parameterization for double wall carbon nanotube model

The parameterization used in this study is based on simulations performed using the MM3 potential, as implemented in the molecular-mechanics package Tinker, version 6.3 [27-30]. A hydrogen-capped, 53 carbon hexagonal graphene flake was used to model the adhered graphitic carbon impurity. Based on HR-TEM analysis, our arc-discharge MWCNTs have inner wall diameters of ~2-3 nm and overall diameters of >15 nm. From our previous simulations of pristine MWCNTs [15], MWCNTs with such small inner diameters and many walls are very rigid-i.e., they cannot fully collapse even when adhered to a graphene substrate—and can thus be assumed to have nearly circular cross-sections. As noted earlier, due to the size limitations of our atomistic model, calculations could not be performed for MWCNTs comparable in sizes to those used in our current and previous experiments [15]. Instead, a (20,0)@(28,0) double-walled carbon nanotube (DWCNT) was chosen as a model nanotube that can provide enough flexibility to reproduce the moderate radial deformations expected for the MWCNTs employed in the experiments while never forming a stable, fully collapsed configuration. Pristine DWCNT of approximately 46 nm length were geometrically relaxed in four configurations: (i) by itself, (ii) with a flake and/or fullerene-like impurity adhered to its surface, and (iii) and (iv) when adhered to the graphitic substrate with and without the impurity. The graphitic substrate was modeled as a graphene ribbon whose geometry was relaxed and then constrained for all further calculations; the edges of the ribbon were hydrogen-capped to remove dangling bonds. All carbon atoms were modeled as sp²-type using the MM3 potential, which includes a well-calibrated expression for van der Waals energy, as described elsewhere [29,31-34].

An interaction energy profile was obtained with relaxation of the [nanotube + impurity + graphene] hybrid structure as a function of the angular position of the impurity around the circumference of the nanotube (see details of simulations and parameterization in the SI, Section S3). The interaction energy of the hybrid was obtained as:

$$Eint_{hybrid} = Eint_{pristine} + \sum S_i \times f(\alpha_i)$$
(1)

where $\operatorname{Eint}_{\operatorname{pristine}}$ is the interaction energy of the pristine tube and the graphitic substrate (see below), S_i is surface area of a pixel containing impurities, α_i is the angular position of that pixel, and $f(\alpha_i)$ is a function defining the per-surface-area potential energy difference between the hybrid structure and pristine nanotube, based on its angular position (see Eqs. (S3–S6) and Fig. S3 in the SI, Section S3). Eint_{pristine} is computed as the difference between the total potential energy of the [nanotube + graphene] hybrid system in the fully adhered state and the sum of the individual potential energies of the constituents in isolation:

$$Eint_{pristine} = U_{DWCNT on graphene} - (U_{DWCNT isolated} + U_{graphene isolated})$$
(2)

For modeling the experimental distribution of the carbon deposit, we rescaled all adhered impurities from the TEM images of large MWCNTs (Fig. 1) to the proportionally smaller size of a (20,0)@(28,0) DWCNT (see further details in the SI,

Section S1). Eq. (1) was used to integrate the energy contributions from the rescaled impurities, and the final normalized adhesion energy values for the hybrids were obtained as

$$Eadh_{hybrid} = \left| \frac{Eint_{hybrid}}{Area_{pristine}} \right|$$
(3)

where $\operatorname{Eint}_{hybrid}$ is the energy calculated from Eq. (1) and $\operatorname{Area}_{pristine}$ is the interaction surface area of the pristine (20,0)@(28,0) DWCNT fully adhered to the substrate. The length of the scaled-down CNT in a fully adhered state is 45.8 nm. A contact width of ~1.50 nm was obtained at 6.68 Å spacing from the surface of the substrate following calculations used in our earlier studies [15].

2.2. Attempts at nanotube purification through chemical treatments

Our survey of the literature identified three methods, previously used for the purification of arc-discharge MWCNTs, that may be promising for the removal of adhered impurities from the surfaces of our arc-discharge MWCNTs: hydrothermal activation [35], bromination [36], or nitric acid treatments [37] followed by oxidation to remove impurities. In these chemical treatments, the impurities in an arc-discharge-produced MWCNT soot are preferentially activated towards oxidation by their greater chemical or intercalative reactivity compared to the highly crystalline outer wall of a MWCNT, followed by removal by calcination (i.e., air-oxidation). As such, we hypothesized that they would be more selective for removing the adhered carbonaceous impurities prior to oxidizing the nanotubes themselves.

2.2.1. Materials and instrumentation

MWCNTs produced by arc discharge (as-produced grade) were purchased from n-Tec (Oslo, Norway) and analyzed by SEM, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and HR-TEM. The MWCNTs were then purified according to the aforementioned published methodologies, as described below, in attempts to remove the strongly adhered carbonaceous impurities. The purified materials were then characterized by SEM, Raman spectroscopy, and HR-TEM to determine the effectiveness of the purification.

Probe-sonication was carried out using a Vibra-Cell[™] VC 505 probe sonicator (500 watts, Sonics & Materials, Inc., Newtown, CT, USA). Bath sonication was carried out using a FS60 bath sonicator (Fisher Scientific, Pittsburgh, PA, USA). Filtration of the chemically treated CNTs was carried out over Anodisc[™] porous alumina filters (0.2 µm pore size, GE Healthcare Bio-Sciences, Pittsburgh, PA, USA). Calcination was carried out in a GSL-1100X tube furnace (MTI Corporation, Richmond, CA, USA) in an alumina crucible. Centrifugation was carried out on a 5804 R Centrifuge (Eppendorf, Hamburg, Germany).

X-ray photoelectron spectroscopy (XPS) and Raman data were collected in the KECK-II/NUANCE facility at Northwestern University using an ESCA Probe (Omicron, Taunusstein, Germany) (Al K α radiation, $h\nu$ = 1486.6 eV) and an Acton TriVista CRS Confocal Raman System (Princeton Instruments, Trenton, NJ, USA), respectively. Raman peaks were fitted using Lorentzian functions with a linear background. In a typical EM experiment, dispersions of CNTs were dropcasted on TEM grids (Lacey carbon type A, Ted Pella, Inc., Redding, CA, USA) and imaged at high resolution at the EPIC/NUANCE facility at Northwestern University using a JEOL JEM-2100 FasTEM instrument (JEOL USA, Inc., Peabody MA, USA) at 200 keV with low exposure time (<20 s) to avoid beam-induced deposition of carbonaceous contamination.

2.2.2. Hydrothermal activation

Following a procedure slightly modified from published literature [35], MWCNT soot (100 mg) was wet-ground in the presence of a small amount of water, probe-sonicated (30 min, 30% amplitude) in ultrapure deionized water (250 mL), and refluxed for 12 h, yielding a suspension of black aggregates. Enough sodium dodecylsulfate (SDS) was added to reach a concentration of 5 g/L, and the suspension was again sonicated (30 min, 30% amplitude) to yield a more homogeneous black, cloudy suspension. This suspension was centrifuged at 3220 rcf for 30 min to precipitate the larger graphitic impurities. The supernatant was collected with a Pasteur pipet and filtered through an Anodisc[™] porous alumina filter, yielding a black film, which was washed copiously with ultrapure deionized water. Complete removal of the SDS surfactant was confirmed by XPS analysis through the absence of a sulfur peak. The remaining MWCNT film was then peeled away from the alumina membrane, dried at 100 °C for 1 h, followed by calcination in stagnant air at 700 °C for 30 min.

2.2.3. Bromination

Following a procedure slightly modified from published literature [36], MWCNT soot (100 mg) was brominated by soaking in liquid bromine (\sim 1 mL) in a sealed vessel (5 mL glass, Teflon capped) at 55 °C for 16 h. The excess bromine was removed from the remaining mixture by heating it to 100 °C under a flow of nitrogen. The remaining residue was suspended in aqueous SDS (200 mL of a 5 g/L solution) and probe-sonicated (30 min, 30% amplitude) to yield a black, cloudy suspension. This suspension was centrifugated at 3220 rcf for 30 min to precipitate the larger graphitic impurities. The supernatant was collected with a Pasteur pipet and



Fig. 2 – XPS analysis of as-produced arc-discharge MWCNTs. The single peak at 298 eV corresponds to the C1s photoelectrons. The absence of other signals confirms that carbon is the only element present in the sample.

filtered through an Anodisc[™] porous alumina filter, yielding a black film, which was washed copiously with ultrapure deionized water to ensure complete removal of the SDS surfactant. The remaining MWCNT film was then peeled away from the alumina membrane, and dried at 100 °C for 1 h, followed by calcination in stagnant air at 700 °C for 1 h.

2.2.4. Nitric acid

Following a procedure slightly modified from published literature [37], larger graphitic impurities were removed from MWCNT soot (100 mg) by probe-sonicating (30 min, 30% amplitude) into aqueous SDS (200 mL of a 5 g/L solution) to yield a black, cloudy suspension. This suspension was centrifuged at 3220 rcf for 30 min to precipitate the larger graphitic impurities. The supernatant was collected with a Pasteur pipet and filtered through an Anodisc[™] porous alumina filter, vielding a black film, which was washed copiously with ultrapure deionized water to ensure complete removal of the SDS surfactant. The remaining purified MWCNT film was then peeled away from the alumina membrane and bath-sonicated (60 min) into nitric acid (70%, 100 mL). The resulting black dispersion was then attached to a refluxing apparatus and refluxed in open air for 1 h, generating a small amount of brown fumes. The resulting oxidized nanotubes were collected by filtration over an Anodisc[™] porous alumina filter, washed copiously with ultrapure deionized water, and then calcined in stagnant air at 700 °C for 1 h.

2.3. Electron microscopy

Each of the chemically treated CNTs were examined by SEM to evaluate the effectiveness of different chemical treatments

in removing non-adhered carbonaceous particles. We were initially concerned that employing different dispersing solvents to prepare the TEM samples may affect the carbonaceous impurities on the walls of the CNTs or result in the deposition of additional impurities. Thus, the as-produced CNTs were dispersed in ortho-dichlorobenzene, acetone, and dimethylformamide by bath-sonication (30 min), dropcasted on a TEM grid, and imaged using HR-TEM. As no differences were observed in the amorphous carbon layer on the surface of these as-produced CNTs, all subsequent samples were dispersed in DMF.

3. Results and discussion

3.1. Design of the computational model

XPS analysis of the as-produced arc-discharge MWCNT soot (Fig. 2) detected only carbon (which was expected, as no other elements were present during their synthesis), suggesting that the adhered impurities are composed of graphitic flakes; fullerene-like structures; amorphous, diamond-like carbon; or a mixture thereof. We determined that these impurities are predominantly composed of graphitic carbon, comprising either graphene flakes or fullerene-like structures, using the evidence presented in the sections below. This is in contrast with CVD-grown MWCNTs, where oxygen is frequently detected in the final product [38], and whose impurities are expected to be much more complex.

3.1.1. Effects of chemical treatments

Because the three chemical treatments that we employed are based on the premise that the impurities in the as-produced



Fig. 3 – SEM and HR-TEM images of as-produced (left) and chemically treated (right) MWCNT samples. As shown, the samples from top to bottom have been subjected to hydrothermal, bromination, and nitric acid treatments, respectively. Additional HR-TEM images of other MWCNTs in each sample are provided in the SI, Sections S4–S7.

MWCNT sample would have higher reactivities compared to the highly crystalline MWCNTs, subjecting the MWCNT-containing soot to these purification techniques can yield information about the structure of these carbonaceous impurities. Under all three methods, the adhered impurities were first "activated" and then removed by oxidation, which remove diamond-like carbon structures more easily than graphitic ones [16], so any impurity that remains must be graphitic in nature. This is indeed the case: while larger, nonadhered impurities can be removed from the samples by every purification treatment technique, as observed by SEM, visualization by HR-TEM still revealed impurities that adhered tightly to the nanotube surfaces (Fig. 3). As such, we conclude that these impurities must have similar reactivities and structures to the MWCNTs and thus must be graphitic in nature.

Analysis of the chemically treated MWCNT samples by XPS (see SI, Section S8 and Fig. S4) showed small amounts of oxygen that can be attributed to partially oxidized impurities, as well as small amounts of silicon and aluminum (likely as SiO_2 and Al_2O_3) that may have resulted from the glassware and alumina equipment used in the treatment process. However, the small amounts of non-oxygen contamination



Fig. 4 – Raman spectra of as-produced MWCNT soot (bottom) and MWCNTs that have been subjected to one of the three chemical treatments. The notation I represents the integrated area of the peaks.

(<1 atom%) suggest that the vast majority of the observed impurities are still carbonaceous in nature.

The Raman spectra (Fig. 4) of the chemically treated samples further supported our conclusion that the strongly adhered surface impurities are primarily graphitic in nature. While the positions of the D (1350 cm⁻¹) and G (1580 cm⁻¹) peaks do not change with chemical treatment, area (I_D) of the D peak increases slightly for the hydrothermally treated MWCNTs, while it decreases slightly for the MWCNTs treated with bromine or nitric acid, possibly due to the greater reactivity of these chemicals towards defect sites. The area (I_{2D}) of the 2D peak (2660 cm⁻¹) significantly changes relative to that (I_G) of the G peak with the nitric acid treatment. The large change observed for the harsh nitric acid treatment can be attributed to changes in orientation [39–41] or folding [42,43] of graphene-like impurities, which are likely to occur during the chemical treatment.

3.1.2. Origin of the adhered graphitic impurities

That the adhered impurities are graphitic in nature is not surprising when one considers the manner in which arcdischarge MWCNTs are produced. During arc-discharge from a carbon cathode, MWCNTs are formed in an arc plasma next to the cathode surface (reaction region) that comprises a mixture of neutral carbon species, singly ionized carbons, and neutral atoms of buffer gas, such as helium. It is well-known that two types of carbon species exist in this plasma [44]: a population of species with a Maxwellian velocity distribution, and a second population containing ionized species that has a unidirectional velocity distribution. The second population nucleates elongated structures (nanotubes) while the first one is responsible for their thickening, resulting in the formation of multishell constructs. Under this scenario, sudden non-homogenous, localized (atom- to nm-sized) increases of the second population within the reaction region would lead to 3D carbon (fullerene-like) clusters as well as capped nanotubes [44]. Not surprisingly, such fluctuation will also produce carbon impurities with graphitic structures similar to those observed in our experiments and form corrugated singlelayer graphitic deposits [45] and polyhedral carbon (or onion-like) structures on the MWCNT surfaces. Such graphitic structures are expected to be as stable against thermal and chemical treatments as the outer walls of arc-dischargegrown CNTs.

We note in passing that the extreme conditions [46] of the arc plasma tend to favor the formation of graphitic species over other less-stable carbon structures. Indeed, conditions similar to those in an arc-discharge chamber (high temperature, vacuum or inert atmosphere) have been utilized for the graphitization of CNTs produced by other methods. For example, high-temperature [47,48] or moderate current-induced heat [49–52] treatments have been applied to heal/ improve the graphitic crystallinity of highly defective or previously broken CVD-grown CNTs.

3.2. Variation of the interfacial properties of MWCNTs due to adhered carbon impurities

We first modeled the adhered carbonaceous impurities as graphene flakes, fullerene-like structures, or combinations of both. Flakes and fullerenes were positioned along the outer wall of the tube (see details in the SI, Part S2) and the resulting structures were relaxed (SI, Fig. S2). As expected, the impurities do not affect the interaction energy when they are located far from the nanotube-graphene interface region. Not surprisingly, local deformations of the nanotube walls were only observed when the flake was positioned directly between the tube and the substrate. Regardless of the shape of the impurity, adhesion would only be improved if the location of the impurity leads to an enlargement of the interaction surfaces between the [tube + impurity] hybrid and the graphene substrate relative to that of a pristine tube. Given this and the small effects that the adhered impurities have on increasing adhesion energy (see discussion below), we choose to simplify our computations by modeling the carbonaceous impurities as solely graphene flakes with constant thickness.

Since the contact width of CNTs during peeling tests is generally not known, adhesion energy is typically reported in "energy" units, or in "energy-per-unit-length" units [13,14,26]. Such units are only appropriate if tests are carried out using single samples whose contact width to the substrate does not vary from test to test. Unfortunately, this does not allow for meaningful comparisons to be made between tests using different nanotubes whose contact widths are different, as disregarded variations of interfacial areas from sample to sample would yield different adhesion energy values. To eliminate this problem in our current study on the effect of adhered carbon impurities, we report our total adhesion energy values in "per interaction surface of pristine tube" units; i.e., we normalize interaction energy per unit area and disregard the change in interfacial area with introduction of impurities.

The adhesion energy of a model [DWCNT + impurity] hybrid to a graphene substrate was obtained as a function of angular position of a single hexagonal graphene-flake impurity around the circumference of the nanotube (see discussions above and SI, Section S3). The obtained energy profile (Fig. 5) suggests that the carbon impurity dramatically decreases the adhesion of the [DWCNT + impurity] hybrid to the graphene substrate if it is located in the interface region. Poor adhesion in this case is attributed to reduction of the interface area as the nanotube is "raised" by the deposit. An opposite (i.e., increased adhesion), but much smaller effect is observed when the impurity is located on top of the tube



Fig. 5 – Top: a schematic description of the model used for parameterization where a single hexagonal graphene-flake impurity is placed around the circumference of the nanotube. Bottom: relative adhesion energy profile as a function of the angular position of the impurity. Inset shows an enlarged initial section of the plot. (A color version of this figure can be viewed online.)

or on its side, which leads to an increase in the interface area due to minor flattening of the tube when it interacts with the impurity (when the latter is far away from the interface), or due to extension of the interface region by the impurity (when the latter is next to the interface). Based on the relative magnitudes of these effects, one can generally expect that the much larger losses in adhesion caused by impurities present in the interface region will dominate over the slight improvements caused by impurities at other locations. This then results in an overall decrease in adhesion energy (Fig. 5). However, it may be possible to find some impurity configurations where the adhesion energy of nanotubes possessing adhered impurities would exceed that of a pristine tube.

Examination of all MWCNT samples, both as-produced and chemically treated ones (see SI, Figs. in Sections S4-S7), revealed a broad variation in surface impurity pattern from MWCNT to MWCNT, as well as along the length and circumference of an individual MWCNT. Thus, it is not possible for us to model the exact interface for a particular experiment. Instead, we selected two representative impurity patterns among those observed for our MWCNT samples (Fig. 6). Structure I is a relatively clean nanotube with impurities localized in one location (Fig. 1a and b), while Structure II corresponds to a nanotube with impurities spread over its whole surface (Fig. 1c and d). To account for the different rotational orientations in which a nanotube can make contact with the surface, each experimentally observed and rescaled impurity patterns was computationally "rolled" around the circumference of our model DWCNT, similar to the protocol that we described above for the model hexagonal flake. In this manner, each set of calculations would yield interaction energy profiles that are representative of all possible orientations of the DWCNT relative to the graphene substrate. The total adhesion energy for each rescaled experimental pattern of impurity (Fig. 6) can then be calculated by summing up the energy contributions from each "pixel" of the modeled DWCNT surface according to the calculated energy profile shown in Fig. 5 (see computational details section and SI, Section S3).

Based on calculations obtained for Structure I (Table 1), we conclude that localized deposits would result in a relatively small scatter in the adhesion energy (standard deviation of 38% and median absolute deviations of 0.38% of the mean/ median value, respectively) during experimental peeling of a [nanotube + impurity] hybrid from a graphene substrate [15]. Due to the large clean tube surface area in Structure I, the impurity resides far from the interface in many tube-on-substrate configurations, yielding adhesion energies that are similar or only slightly higher than those obtained for a pristine tube. Not surprisingly, the scatter in adhesion energy for Structure II is much larger (standard deviation of 68% and median absolute deviation 64% of the mean/median value, respectively) due to the presence of impurities near the nanotube-substrate interfaces in nearly all configurations. We then combined Structures I and II end to end as two segments of a DWCNT with a much more complex pattern of deposit. By keeping one segment fixed and rotating the other segment, we were able to span all possible relative orientations. In this set of structures (Structure I + II), the standard deviation in measured adhesion energy due solely to variation in surface-adhered impurities is 34%, while the median absolute deviation is 20%. These values are close to the scatter reported in experimental measurements of surface energy



Fig. 6 – (Top) Histograms showing population of adhesion energies for different configurations of hybrid-substrate interface region. The bin size is 0.01 J/m². Median and mean values are graphed on the left and right, respectively. (Bottom) Schematic representation of the surface impurity patterns Structures I and II used for calculating the adhesion energy values. (A color version of this figure can be viewed online.)

Table 1 – Modeled mean adhesion energies (J/m²), standard deviation values (J/m²), median adhesion energies (J/m²), and median absolute deviations (J/m²). Statistical analyses were carried out for Structure I, Structure II, and a combination of both structures, each based on one separate data set. We include the median and median absolute deviation because the distributions are not normal, and standard deviation is not capable of fully describing the scatter.

Structure	Mean adhesion energy (J/m²)	Standard deviation (J/m ²)	Median (J/m²)	Median absolute deviation (J/m ²)
I	0.07983	0.03056	0.09899	3.79×10^{-4}
II	0.04778	0.03226	0.04495	0.02869
I + II	0.06382	0.02203	0.064	0.013

[15] using tubes that are similar to those reported in the current study, supporting our initial conjecture that surfaceadhered impurities can significantly alter the properties of the underlying CNTs.

We note in passing that similar to the simple [DWCNT + hexagonal graphene - flake impurity] model that we initially discussed in Section 3.2, the adhesion of our rescaled [(20,0)@(28,0) DWCNT + impurity] system to a graphene substrate always yields mean energies that are lower than those for the pristine nanotube adhering to the substrate. As observed for that simple system, certain configurations, particularly for Structure I, in our rescaled hybrids can also have improved adhesion to the substrate compared to the pristine nanotube (0.0935 J/m²); however, the improvement is very small. In such configurations, the impurity is predominantly located atop or on the side of the nanotube, rather than at the interface. Together, these data suggest that adhered impurities cannot be disregarded when processing experimental data or when developing computational models.

4. Conclusions

In summary, we have presented evidence that surfaceadhered impurities comprise a component that cannot be ignored in experiments involving single nanotubes and their interfaces with a second surface. We found computationally that the adhesive interactions of a CNT-graphene interface can be significantly altered by the presence of carbonaceous impurities. In particular, we find that they can cause over 30% of the scatter in interaction energies, similar in magnitude to the scatter reported in experimental measurements [8,14,15,18–20].

Although a number of chemical treatments can be effective in removing the discrete larger graphitic particles from a sample of as-produced arc-discharge MWCNTs, none of these techniques are effective for removing the stronglyadhered surface contamination as observed by HR-TEM. These strongly-adhered carbonaceous impurities are likely graphitic in nature, and thus are very similar to the MWCNT surfaces, both in chemical reactivity and thermal stability. As such, their presence should not be ignored when CNTs are utilized in applications that are affected by surface interactions, such as those between CNTs in nanocomposite fibers and yarns. Before a strategy can be developed for removing these strongly-adhered surface impurities, their presence must be taken into account in any study where the interfaces formed by nanotubes play an important role.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2014.07.069.

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