Single functional group interactions with individual carbon nanotubes

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Carbon nanotubes¹ display a consummate blend of materials properties that affect applications ranging from nanoelectronic circuits² and biosensors³ to field emitters⁴ and membranes⁵. These applications use the non-covalent interactions between the nanotubes and chemical functionalities⁶, often involving a few molecules at a time. Despite their wide use, we still lack a fundamental understanding and molecular-level control of these interactions. We have used chemical force microscopy⁷ to measure the strength of the interactions of single chemical functional groups with the sidewalls of vapour-grown individual single-walled carbon nanotubes. Surprisingly, the interaction strength does not follow conventional trends of increasing polarity or hydrophobicity, and instead reflects the complex electronic interactions between the nanotube and the functional group. Ab initio calculations confirm the observed trends and predict binding force distributions for a single molecular contact that match the experimental results. Our analysis also reveals the important role of molecular linkage dynamics in determining interaction strength at the single functional group level.

Understanding the nature of the interactions between carbon nanotubes (CNTs) and individual chemical functional groups is a prerequisite for the rational engineering of future generations of sensors⁸ and nanodevices⁹ that will rely on single-molecule coupling between components. In principle, this goal can be accomplished by a direct measurement of the adhesion force experienced by an individual molecule at the CNT surface. However, the small size of a nanotube makes such measurements challenging and forces researchers to rely on modelling¹⁰, indirect measurements¹¹ and large microscale tests¹². To date, very few experimental studies have attempted direct measurements of interaction forces between ensembles of functional groups and single-walled CNTs (refs 13, 14), and no study has been performed on a single molecule level in a controlled environment. Multiple functional group measurements are also much too complex for direct comparison with computer

simulations, so researchers have had to use continuum models¹⁵, precluding molecular-level understanding of the interactions.

We have performed a direct measurement of functional group interactions with carbon nanotubes using atomic force microscope (AFM) probes functionalized with specific chemical groups. This technique, known as chemical force microscopy⁷, enables direct characterization of intermolecular forces. To achieve a true single functional group interaction measurement with this technique, it was necessary to minimize the probe–nanotube contact area (Fig. 1a). All the measurements were performed in toluene to eliminate capillary forces and solvation forces, which can obscure true molecular interactions^{16,17}. The critical step was to make use of the very sharp topography of individual, isolated, high-purity vapour-grown CNTs (Fig. 1b, inset) with a narrow distribution of diameters centred at 1.3 nm (Fig. 1b).

The high curvature of the CNTs, coupled with controlled chemical modification of the probe, enabled us to obtain a reproducible and consistently small tip-nanotube contact area, which would not be achievable for measurements on flat substrates or bundled nanotube surfaces. Hertzian mechanics18 estimates a nearly constant tip-nanotube contact area of 0.33 ± 0.03 nm² for the measurements. If silane molecules at the end of the AFM tip retain the same density as in a close-packed monolayer on a flat surface (0.2-0.3 nm² per group)¹⁹, then this contact area corresponds to an area occupied by a single terminal group at the very end of the modified AFM tip. The remarkable consistency of the rupture forces that were measured for each of the functional groups also supports this conclusion, as even occasional involvement of the second or third chemical groups would yield significantly scattered rupture force values by introducing very large (factor of 2 to 3) variations, well exceeding the experimental deviations observed in our measurements.

We used a closed-loop AFM (see Methods) to position the probe tip reproducibly over individual CNTs or the bare silicon substrate. Adhesion forces collected on the CNT surface (Fig. 1d) were clearly distinct from the forces collected on the substrate



Figure 1 Measurement setup, nanotube characterization, and site-specific force spectroscopy. a, Schematics of the measurement showing an AFM tip functionalized with silane molecules terminating in specific functional groups contacting isolated individual CNTs on the sample surface. **b**, Histogram of the diameters of CNTs measured from the AFM images. The solid blue line corresponds to a gaussian fit of the histogram. The average diameter of the nanotubes is 1.3 ± 0.5 nm; the gaussian fit peaks at 1.1 nm. Inset: A tapping-mode AFM image of the as-grown sample surface showing uniform coverage of the isolated individual nanotubes. **c**, **d**, Interaction forces measured in toluene in different areas of the sample using an NH₂-terminated probe: a histogram of adhesion forces collected on the silicon oxide surface (**c**) and a histogram of adhesion forces collected on the CNTs (**d**).

(Fig. 1c). This result indicates that our force measurements on CNTs were site-specific, and that instrument precision was sufficient for placing the AFM probe directly over the CNT. In addition, it shows that our samples were free of large levels of carbon contamination from nanotube synthesis that could have masked the true interaction forces.

Site-specific force measurement was performed using AFM tips modified with short-chain silanes, which differed only in the terminal functional group R ($R = NH_2$, CN or CH₃). These functionalities were chosen to represent the major classes of the interacting groups: an electron donor, an electron acceptor and a weak van der Waals interacting group. Adhesion force histograms show that the interaction forces varied significantly from one functionality to the next (Fig. 2a,c,d), with the amine-terminated probes providing the strongest adhesion, and the cyano group providing the weakest adhesion, similar to the trends observed previously for multiple group interactions¹⁴. To confirm that the measured forces reflect specific functional group interactions, we compared the interaction forces measured with probes functionalized with n-butylsilane and octadecylsilane. Both of these molecules should produce methyl-terminated probes (in the case of octadecylsilane functionalization, the methyl group was anchored to the probe tip with a much longer hydrocarbon chain), and both probes produced similar interaction forces that were clearly distinct from the forces obtained for the rest of the functional groups (Fig. 2).

The measured interaction strengths do not follow any obvious trend, such as increasing functional group hydrophobicity or



Figure 2 Comparison of the measured and calculated binding strength for the interactions of chemical functional groups with CNTs. a-d, Histograms of binding forces measured between individual CNTs and AFM tips functionalized with NH₂ (**a**), CH₃ (**b**,**c**), and CN (**d**) functionalities in toluene. Vertical dashed lines indicate the position of F_c , corresponding to the force at which the predicted barrier to rupture disappears. Solid blue lines correspond to the binding force distributions predicted by equation (1) using the calculated interaction potentials. Insets: Calculated interaction energies as a function of the tip distance (red open circles) and Morse potential fits (solid black lines) for each system. Rupture force distributions in **b** and **c** were fit using the same interaction potential as the silanes used to modify the probes terminated in the same $-CH_3$ functional group.

polarity. To explore the origin of the measured interaction forces, we performed *ab initio* simulations of the interactions of functional groups with the sidewall of a (14,0) ziz-zag CNT that had the same diameter as the nanotubes used in the experiment. The calculation results (Table 1) highlight a strong dependence of the interaction strength on the electronic structure of the interacting molecule/CNT system. A closer look at two

different modes of the $-NH_2$ group interactions with the CNT (either through an H atom or a lone electron pair) reveals strong electrostatic contributions to the interaction and striking differences in the charge polarization (Fig. 3). The interaction through the lone pair causes a positive polarization charge on the CNT. It induces a depletion charge in the underlying carbon ring, generating an attractive force between the negatively charged lone pair and the nanotube (Fig. 3a). The opposite situation occurs when the tip interacts through the hydrogen atom, which is partially positively charged (Fig. 3b).

This analysis suggests that small amounts of charge transfer from the functional group to the nanotube and the resulting deviations of the CNT from perfect electronic neutrality are important for understanding the results of our force spectroscopy measurements. This is not entirely surprising, as electronic effects often determine the chemical reactivity of CNTs (refs 20, 21). Because the CNTs were immersed in toluene during the force spectroscopy measurements, it is important to consider the effect of the medium on the charge state of the CNTs. Several observations point to the toluene molecules inducing a partial negative charge on the CNT sidewalls. Recent experiments have shown that both the capacitance and the conductance of a CNT network are sensitive to the presence of dilute concentrations of a wide range of vapors^{22,23}. A negative shift in the threshold voltage upon exposure of CNT transistors to aromatic compounds has been observed²⁴ (also, A. Star, personal communication). Our ab initio simulations of the interaction of a single toluene molecule with the nanotube walls (see Supplementary Information for details) show that equilibrated toluene molecules reside flat on the CNT wall, with $\pi - \pi$ interactions stabilizing the complex by 0.34 eV. Such stabilization may also explain reports of strong charge transfer interactions between arylnitrile polymers and CNTs (ref. 25). In our simulations, a small hybridization between the highest occupied molecular states of the nanotube and the toluene also caused a small negative charge of about 0.05 electron per toluene molecule to appear on the CNT walls. Finally, our Kelvin probe force microscopy (KPFM) imaging of CNTs before and after exposure to the toluene solvent (see Supplementary Information for details) shows that changes in the CNT work function upon exposure to the solvent are consistent with the increased negative charge on the CNTs (see Supplementary Information, Fig. S1).

The order of the binding energies calculated for the interactions of different functional groups with negatively charged CNTs matches the order of the rupture forces observed in the experiment (Table 1), unlike the interaction energies calculated for the positively charged and neutral nanotubes. Moreover, the single-molecule scale of our measurements permits direct quantitative comparison with the simulation results (Fig. 2). The naïve but widely used approach is to compute binding forces as the maximum gradient of the simulated interaction potentials. However, thermal fluctuations produce a distribution of rupture forces that, for most experimental velocities, fall below this value²⁶. A rigorous formalism that predicts the rupture force distribution based on the shape of the interaction energy profile along the pulling coordinate has been developed²⁷:

$$P(F) = P_0 \varepsilon^{1/2} \exp\left\{-\frac{U_c}{k_B T} \varepsilon^{3/2} - \frac{k_B T \omega_c^2 m F_c}{U_c 3 \pi \gamma k \nu} e^{-\frac{U_c}{k_B T} \varepsilon^{3/2}}\right\}$$
(1)

where k and v are respectively the cantilever spring constant and pulling velocity, γ is the damping coefficient of the system and $k_{\rm B}$ is Boltzmann's constant. The parameters $U_{\rm c}$ and $\omega_{\rm c}$ are the characteristic energy and oscillation frequency of the unperturbed

Table 1 Calculated interaction energies (ΔE) and equilibrium distances (d_{eq}) for the model AFM probes interacting with neutral, positively and negatively charged CNTs. For the $-NH_2$ functionalized probe the listed parameters are calculated for the interaction through the H atom (H) and through the lone pair (LP).

| Functional group | Negatively charged CNT | | Positively charged CNT | | Neutral CNT | |
|-----------------------|------------------------|---------------------|------------------------|---------------------|-----------------|---------------------|
| | ΔE (eV) | d _{eq} (Å) | ΔE (eV) | d _{eq} (Å) | ΔE (eV) | d _{eq} (Å) |
| -CN | -0.06 | 2.9 | -0.21 | 2.9 | -0.15 | 2.9 |
| -CH ₃ | -0.09 | 2.4 | -0.06 | 2.5 | -0.09 | 2.5 |
| $-NH_{2}$ (H) | -0.21 | 2.1 | -0.09 | 2.1 | -0.15 | 2.1 |
| -NH ₂ (LP) | -0.11 | 2.8 | -0.25 | 2.8 | -0.19 | 2.8 |

Table 2 Measured rupture forces and calculated interaction parameters for binding of functional groups to a negatively charged CNT sidewall.

| Probe functionality | Mean rupture force (pN) | Morse potential parameters | | | Damping constant, γ (10 ⁻⁴ kg/s) |
|-----------------------------|-------------------------|----------------------------|-----------------------------|---------------------|--|
| | | $U_{\rm o}~(k_{\rm B}T)$ | <i>b</i> (Å ⁻¹) | d _{eq} (Å) | |
| $-(CH_2)_3 - NH_2$ | 189.8 ± 79.5 | 7.60 | 0.899 | 2.8 | 4.87 ± 0.47 |
| $-(CH_{2})_{3} - CH_{3}$ | 64.0 ± 39.9 | 4.19 | 0.745 | 2.4 | 1.34 ± 0.14 |
| $-(CH_2)_2 - CN$ | 9.0 + 15.1 | 1.56 | 1.430 | 2.9 | 2.47 + 0.73 |
| $-(CH_2)_{17}^{2/3} - CH_3$ | 36.5 ± 31.6 | 4.19 | 0.745 | 2.4 | 0.30 ± 0.02 |

The parameters used in equation (1) were calculated by fitting the Morse potential function $U(x) = U_0[1 - \exp(-2b(x - d_{e0}))]^2$ to the calculated interaction profiles and d_{eq} values to find²⁷ $F_c = bU_0$, $U_c = U_0(1 - g)^{-1/2}$, $\omega_c = 2bU_0^{1/2}/(m^{1/2})(1 - g)^{1/4}$, with $g = 3kU_0/(4F_c^2)$.

bond, respectively, *m* is the effective particle mass, $\varepsilon = 1 - F/F_c$ is the reduced bias relative to the critical force F_c at which the energy barrier vanishes and P_o is a normalization constant. We note that all parameters in equation (1) except for the damping coefficient γ are determined either directly from experiment or from the calculated interaction potentials (Fig. 2, insets). To determine the damping coefficient we fit the measured rupture force distributions to equation (1). Remarkably, damping coefficient values for the probes modified with the short-chain silanes all fall within a factor of 2.2 of the average value of $2.9 \times 10^{-4} \text{ kg s}^{-1}$, and the probe functionalized with the long-chain silane shows an order of magnitude lower damping coefficient (Table 2). Even more remarkable is the close fit of the calculated force distributions to the experimental data; the calculated distributions closely reproduce the measured distributions for all functional groups (Fig. 2).

These results underline the importance of *ab initio* simulations with coupled single-molecule level measurements for understanding and predicting interaction strength on a single functional group level. As multiple connections would produce much broader distributions than that predicted by equation (1), this comparison provides additional corroboration for our conclusion that adhesion measurements are indeed probing the interactions of a single functional group with the nanotubes. A small portion of the rupture events observed for each functional group produced rupture forces that were higher than the critical force F_{c2} as reflected in the small tails in the range of high binding forces in the rupture distributions in Fig. 2. These tails could reflect different orientations of the functional groups on the probe tip, variations in the local environment or an occasional contact of the probe with defects on the CNT surface, which may produce stronger binding than interactions with defect-free sidewalls²⁸.

Why were the forces measured for probes functionalized with n-butylsilane and octadecylsilane (Fig. 2b,c) not identical? This comparison points to an important role played by the linker. As expected for short rigid linkers, the damping coefficients determined for the probes functionalized with short silanes (Table 2) match the damping coefficients measured for an AFM cantilever in close proximity to a surface²⁹. Connecting the functional group to the cantilever with a much longer linker should decrease the effective damping coefficient, increase the spontaneous escape rate, and result in a smaller rupture force.



Figure 3 Electron density analysis of the NH₂-functionalized tip interacting with a (14,0) CNT sidewall. a,b, Ball and stick model of the equilibrium structure for the NH₂-functionalized tip interacting with a neutral CNT through the lone pair (a) and the H atom (b). Grey, dark blue, green and white spheres correspond to C, N, Si and H atoms, respectively. Negative and positive polarization charges appearing in the interacting nanotube/tip system are represented by the yellow and red surfaces, respectively. This charge polarization illustrates the trend observed in the experiment and in the calculations: negative charge on the CNT weakens the interaction with the -CN functional group while reinforcing the interactions with the -CH₃ and -NH₂ groups.

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Indeed, forces measured with an octadecylsilane probe (Fig. 2b) were smaller than forces measured using an n-butylsilane probe, and the octadecylsilane probe had an almost four times lower value for the damping coefficient. This is another example of using a combination of single functional group force spectroscopy measurements and *ab initio* simulations as a unique tool for understanding nanoscale interactions. This approach could have important implications for the design of novel CNT composite materials, for the design of new single-molecule-scale sensors, as well as for the development of new chemical strategies for nanotube functionalization.

METHODS

AFM PROBE FUNCTIONALIZATION AND CNT SYNTHESIS

Clean silicon AFM probes (Sharpened Microlevers, model MSCT from Veeco, cantilever A) were cleaned in piranha solution for 45 min and then incubated in anhydrous toluene solutions of either (3-aminopropyl) trimethoxysilane, octadecyltrichlorosilane, n-butylsilane or (3-cyanopropyl) trimethoxysilane under a nitrogen-purged glove box to obtain $-NH_2$, $-CH_3$ and -CN functionalization in accordance with known procedures³⁰. The CNTs were synthesized using a 1-inch chemical vapour deposition system. Briefly, we dipcoated colloidal iron catalyst particles onto piranha-oxidized silicon wafers and grew CNTs at 850 °C in a tube furnace using a 600 s.c.c.m.:400 s.c.c.m.:5 s.c.c.m. flow mixture of Ar:H₂:C₂H₄ feedstock gases. This process consistently yielded separated individual clean single-walled CNTs, well-dispersed on the silicon wafer surface (Fig. 1b, inset). These samples were used for the force spectroscopy measurements without further treatment.

SITE-SPECIFIC FORCE SPECTROSCOPY

We performed all measurements using a closed-loop AFM (MFP-3D, Asylum Research). All measurements were carried out in a fluid environment using an inert organic solvent (toluene) to eliminate capillary loads¹⁶. We modified the surface of our tips using alkylsilane monolayers, which do not degrade the probe sharpness to the same extent as the more common gold/thiol modification, where a thicker gold layer is evaporated onto an AFM probe³⁰. The probe tip size used in our experiments was 18 + 2 nm, as determined by scanning a reference gold colloid standard after the measurements. To attain the maximum probepositioning stability and eliminate any possibility of sample drift caused by a fluid cell O-ring, all AFM measurements were performed using an open fluid cell with a toluene drop sandwiched between the fluid cell and the sample surfaces. To avoid drying we periodically replenished the drop by adding small amounts of toluene using a pipette tip. To ensure accurate probe positioning during force spectroscopy measurements, we first performed progressively smaller tappingmode scans of the area of interest (typically until we reached 100 nm \times 100 nm scan size). We then switched the microscope to contact mode and collected force-distance curves at prepositioned points along the nanotube. We note that the diameters of our nanotubes were much smaller than the AFM tip diameter and consequently the nanotube 'reverse-imaged' the probe tip. This geometry relaxes the probe placement accuracy requirements: a simple geometrical calculation (see Supplementary Information for details) shows that to contact a nanotube of radius r, a probe of radius R only has to land within a distance of $2(Rr)^{1/2}$ from the centre of the nanotube. For our experiments this distance corresponds to 6.8 nm, well within the accuracy of modern AFMs. The reported interaction force histograms comprise data from more than 300-400 individual pull-off measurements collected at multiple points on multiple nanotubes.

For the contact mechanics estimation of the probe-sample contact area, we assumed the value of the compression axial modulus of the nanotube to be approximately 150 GPa (ref. 31). This high in-plane strength ensured that any compression of the nanotube would be negligible, even under the highest load of 1.2 nN (corresponding to local pressures below 4 GPa) used in our work. High compression strength also ensures that mechanical indentations do not induce any deformation and thus do not alter the electronic properties and overall structure of the CNT significantly in the course of the measurement. The calculated contact areas (nm^2) were 0.34 (-CN), 0.36 (-CH₃) and 0.31 (-NH₂).

AB INITIO SIMULATIONS

All pull-off computational experiments were carried out using the density functional theory within the local density approximation; the calculations were

performed using a pseudo-potential plane wave formulation of ab initio molecular dynamics (MD)³², as implemented in the GP and Qbox codes written by F. Gygi (LLNL 1998-2003). Electron/ion interactions were treated with norm-conserving pseudopotentials of the Hamann type³³, and Kohn-Sham orbitals were expanded in plane waves up to an energy cutoff of 60 Ry. The integration over the Brillouin zone was performed using only the Γ point. All calculations considered the (14,0) nanotube, which has a diameter of 1.1 nm. We chose this nanotube because its size is close to the diameter of the nanotubes in our samples (Fig. 1), and because it is semiconducting, similar to most of the nanotubes in our sample. We modelled the AFM tip with a SiH₃-CH₂-X molecule, where X represents the terminal chemical functional group and a Si atom represents the AFM tip. The structural simplicity of the attached molecules allowed us to fully explore functional group orientation and tip/nanotube alignment in our calculations and obtain an accurate potential energy curve for each functional group. The pull-off experiment was simulated by slowly increasing the nanotube-silicon atom distance, while simultaneously optimizing the full structure of the nanotube and the functional group. To compute the parameters used in equation (1), we fit the calculated interaction potentials with a Morse potential²⁴ (Fig. 2, insets).

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Author contributions

A.N., V.V.T., G.G. and J.C.G. conceived the experiments. R.W.F, M.C.L., A.B.A. and A.N. performed the experiments, and analysed the data. G.C., J.C.G. and G.G. performed computer simulations. A.N., R.W.F., G.C. and G.G. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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