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Carbon Nanotubes Covalently Attached to Functionalized Surfaces Directly through the Carbon Cage

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Abstract

The covalent attachment of nonfunctionalized and carboxylic acid-functionalized carbon nanotubes to amine-terminated organic monolayers on gold and silicon surfaces is investigated. It is well established that the condensation reaction between a carboxylic acid and an amine is a viable method to anchor carbon nanotubes to solid substrates. The work presented here shows that the presence of the carboxylic group on the nanotube is not required for attachment to occur, as direct attachment via the substrate amine and the nanotube cage can take place. Scanning and transmission electron microscopy and atomic force microscopy confirm the presence of carbon nanotubes in intimate contact with the surface. X-ray photoelectron spectroscopy is utilized to compare the surface chemistry of the functionalized and nonfunctionalized carbon nanotubes and is supported by a computational investigation. Ion fragments attributed to the direct attachment between the surface and carbon nanotube cage are detected by time-of-flight secondary ion mass spectrometry. The overall attachment scheme is evaluated and can be further used on multiple carbonaceous materials attached to solid substrates.

Graphical abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b02641. Density functional theory description and models, full text for ref 46, ToF-SIMS spectra within the range of 200–400 *m/z*, C 1s XPS spectra, and SEM micrograph of the control silicon sample to demonstrate that sonication by itself is not sufficient to induce the chemical attachment of CNTs (PDF)

INTRODUCTION

Since the initial identification of and reports on carbon nanotubes,^{1,2} their properties have spurred a flurry of intense studies because of their unique structure and characteristics. The chemical reactivity and the optical, mechanical, and electronic properties of carbon nanotubes (CNTs) have resulted in the integration of these materials into various fields and applications, including sensors,^{3–5} nanoelectronic devices,⁶ hydrogen storage,^{7,8} and field emission devices.^{9,10} For such applications, the ability to control and fine-tune the attachment and placement of carbon nanotubes onto a solid substrate is necessary.

The immobilization of CNTs onto gold substrates, typically following the formation of alkylthiol self-assembled monolayers (SAMs), has been amply reported in the literature. Functionalized carbon nanotubes can be anchored to these thiolated gold surfaces via condensation or amide formation.^{11–13} The long-term stability of the CNT–substrate interface involving thiol–gold linkages may be a concern, however, because of thermal instability and photooxidation of the SAM.¹⁴ For applications in which these challenges may pose problems, the gold–thiol interface can be circumnavigated by the sturdy attachment of CNTs onto silicon substrates. Several examples in the literature highlight CNT attachment to amine- or hydroxyl-modified silicon surfaces.^{15–17} To avoid the layer of oxidized silicon, alternative methods involving the direct hydrogenation of silicon followed by modification with aliphatic alkenes for further reaction with carbon nanotubes have been proposed.¹⁸ Examples of the attachment of carbon nanotubes to other surface materials, such as polymers¹⁹ and ITO glass,²⁰ have also been reported.

Thus, most of the previous methods in the literature describing the covalent attachment of carbon nanotubes rely on interactions between the substrate surface species and functional groups (e.g., carboxylic acid) on the carbon nanotubes. In most cases, the functional group is present only on the ends of the CNTs, rather than along the length (with the exception of defects). This is ideal for applications in which vertically aligned CNT assemblies are desired; however, in cases where a very high degree of intimate covalent contact is required between the CNTs and substrate, bonding between the substrate and the cage of the CNT may be preferred. It has been shown that electron transfer through CNTs attached to a gold substrate via self-assembled monolayers is influenced by electrons tunneling through the SAMs.²¹ The presence of functional groups bound to a carbon nanotube can also impact the charge transport through the CNT, depending on the nature of the bonding involved.^{22,23} These changes are desired in some cases, such as in chemical sensor development;²⁴ in other

cases, however, it may be preferable for the intrinsic electronic properties of the nanotube to be preserved.

Interestingly, the surfaces of CNTs are rarely the subject of direct chemical modification. The inner surfaces of nanotubes are considered to be inert, and in fact these materials are commonly used to provide the cage effect for highly controlled processes inside the nanotubes.^{25–27} On the other hand, a number of adsorbates have been shown to react with the outside surface of CNTs.^{28–31} The question is whether the reactivity of the outer surface of carbon nanotubes without additional chemical functionalities could be explored to staple them covalently to chemically functionalized surfaces. This approach has been suggested for similar systems.³² The covalent bonding between the cage of a C₆₀ buckyball and solid flat semiconductor substrates has been reported and reviewed in detail,^{33–36} with one of the examples of such interactions involving the direct attachment of the C₆₀ and amine-terminated self-assembled monolayers.^{37–39} In another study, the attachment of [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM), structurally similar to the buckyball, to an amine-modified silicon surface showed that whereas both the attachment through the ester to form an amide and the attachment through the cage to form a secondary amine are viable, the latter is actually more favorable.⁴⁰ It stands to reason, then, that the direct attachment of carbon nanotubes through the cage, regardless of the presence or absence of other functional groups, might occur in a similar manner, in addition to the expected attachment through those functional groups. In the present work, the attachment of nonfunctionalized carbon nanotubes to amine-modified gold and silicon substrates, as summarized in Figure 1, is demonstrated. Microscopy techniques confirm the presence of the CNTs on the surfaces after washing and sonication to remove physically adsorbed CNTs. X-ray photoelectron spectroscopy (XPS) coupled with density functional theory (DFT) calculations are used to evaluate the chemistry of the system. Of course, unlike for the previously reported C₆₀ system,⁴⁰ the final point for analyzing CNT attachment chemistry is not well-defined. Finally, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to identify fragments from CNT attachment to the surface and to compare the attachment of nonfunctionalized CNTs and carboxylic acid-functionalized CNTs to these surfaces.

EXPERIMENTAL METHODS

Experimental Details

Materials—Phosphorus-doped, n-type, double-side-polished Si(111) wafers (Virginia Semiconductor Inc., >0.1 Ω-cm resistivity, 500 μm thickness) and prefabricated gold-coated wafers (1000 Å gold thickness on a silicon wafer support with a titanium adhesion layer, Sigma-Aldrich) were used as substrates. All chemicals were reagent grade or as indicated: nonfunctionalized carbon nanotubes (NF-CNTs) (>90%, 1–4 nm diameter, cheap-tubes.com), single-walled carboxylic acid-functionalized carbon nanotubes (COOH-CNTs) (95%, 1–2 nm diameter, Nanostructured & Amorphous Materials, Inc.), nitrogen (Praxair, boiled off from liquid nitrogen tank), argon (Keen Compressed Gas, research purity), hydrogen peroxide (Fisher, 30% certified ACS grade), ammonium hydroxide (Fisher, 29% certified ACS plus grade), hydrochloric acid (Fisher, 37.3% certified ACS grade), buffer-HF improved (Transene Company, Inc.), 11-chloro-1-undecene (Aldrich, 97%), trifluoroacetic

acid (TFA) (Aldrich, 99%), potassium phthalimide (Fluka, 99.0%), hydrazine hydrate (64%, Acros Organics), di-*tert*-butyl dicarbonate (Sigma-Aldrich, 99%), dichloromethane (Fisher, 99.9%), petroleum ether (Fisher, Certified ACS), ethyl ether (Fisher, Laboratory grade), cysteamine hydrochloride (98%, Acros Organics), propylamine (Aldrich, 98%), 2-dimethylamino ethanethiol hydrochloride (Acros, 95%), *N,N*-dimethylformamide (DMF) (certified ACS, Fisher Scientific), methanol (Fisher, 99.8%), and ethanol (Decon Laboratories, 200 proof). The deionized water with 18 M Ω ·cm resistivity used to rinse the surfaces and containers was from a first-generation Milli-Q water system (Millipore).

Monolayer Formation on Silicon—The *tert*-butoxycarbonyl (t-BOC)-protected 11-amino-1-undecene (AUD) was prepared by standard organic synthesis methods.^{39,41} A 5 mL quantity of a solution of the t-BOC-protected 1-amino-10-undecene was placed in a 25 mL flask fitted with a reflux condenser and kept under flowing N₂. The solution was deoxygenated with dry N₂ for at least 1 h. The hydrogen-modified Si(111) surface was prepared by a modified RCA cleaning procedure.^{42–44} The flask was immersed in an oil bath, and the solution was maintained at 110 °C for 2 h under slow N₂ flow. The sample was then removed from the solution and cleaned in petroleum ether (40–60 °C), methanol, and dichloromethane. Afterward, treating the surface with 25% TFA in dichloromethane for 1 h was followed by a 5 min rinse in 10% NH₄OH to remove the t-BOC protecting group and to form the primary-amine-terminated surface. The surface was then rinsed with deionized water and dried with N₂.

Monolayer Formation on Gold—A prefabricated gold-coated wafer was annealed to 400 K for 2 h at 10^{–5} Torr. The wafer was immersed in a solution of 2 mg cysteamine hydrochloride in 10 mL of DMF for 24 h, followed by rinsing with DMF to remove physically adsorbed cysteamine.

Carbon Nanotube Attachment—A 50% (w/v) solution of either single-walled nonfunctionalized carbon nanotubes or single-walled carboxylic acid-functionalized carbon nanotubes in DMF was prepared and sonicated in ice water for at least 1 h to achieve good dispersion. To promote attachment between the carbon nanotubes and functionalized gold and silicon surfaces, the cysteamine-covered Au surface and 11-amino-1-undecene-modified Si surface were immersed in the CNT/DMF solution and sonicated (40 kHz, Branson 1510) in an ice water bath for 3 h. They were then rinsed with methanol and deionized water and dried in a stream of nitrogen. To confirm that this preparation procedure does not induce the reaction with a chemically inert monolayer, a control experiment with the CNT reaction with (t-BOC)-protected AUD was performed, and the resulting SEM micrographs confirming this assessment are presented in the Supporting Information section.

Characterization Techniques

Microscopy—A Zeiss Auriga 60 scanning electron microscope (SEM) with an accelerating voltage of 3 kV was used, and images were collected with a secondary electron (in-lens) detector at a working distance of 5.0 mm. Atomic force microscopy (AFM) with a Veeco Multimode SPM with a Nanoscope V controller was performed in tapping mode. Tap300Al-G tips (Budget Sensors) with a force constant of 40 N/m and a drive frequency of

300 kHz were used, and the images were analyzed using Gwyddion software.⁴⁵ The average diameter of the individual nanotubes was independently confirmed via a JEOL JEM-3010 transmission electron microscope (TEM) using an incident electron energy of 300 keV.

X-ray Photoelectron Spectroscopy—Spectra were collected with a Thermo Scientific K-Alpha⁺ instrument equipped with a monochromatic Al K α source ($h\nu = 1486.6$ eV) at a takeoff angle normal to the surface and a base pressure of 5×10^{-9} mBar. Survey spectra were collected over the energy range of 0–1000 eV, with a 100 eV pass energy at 1 eV/step and a 10 ms dwell time. High-resolution spectra were collected over a range of 20 eV, with a 58.7 eV pass energy at 0.1 eV/step and a 50 ms dwell time. The number of high-resolution spectra collected ranged from 3 to 50 scans, depending on the spectral region being analyzed. The Au 4f_{7/2} peak at 83.8 eV was used to calibrate the spectra collected on gold substrates, and the most intense C 1s peak at 284.6 eV was used to calibrate the spectra collected on silicon substrates. CasaXPS (version 2.3.16) was used for data processing and peak fitting.

Computational Details—Calculations were performed using the Gaussian 09⁴⁶ suite with the B3LYP^{47,48} functional and LANL2DZ^{49,50} basis set. Geometry optimization and prediction of the core-level energies for N 1s were performed. A single-walled carbon nanotube structure with (10, 0) chirality was built using TubeGen3.4⁵¹ and imported into Gaussian 09 for optimization. This chirality results in semiconducting CNTs, and was chosen to represent the CNTs used experimentally in this study. The zigzag structure is commonly used for computational studies of carbon nanotubes.^{52–54} The functionalized monolayer on gold was modeled by cysteamine on a single gold atom, and the functionalized monolayer on silicon was modeled by 11-amino-1-undecene on a Si₄H₉ cluster. For calculations involving direct amine attachment to the cage of the carbon nanotube, two possible geometries were optimized. In the first (labeled parallel or || in this work), the amine dissociates across a C=C bond in the CNT cage that lies parallel to the direction of the carbon nanotube. The second (labeled nonparallel or $\perp$) geometry involves the amine dissociated across a bond that does not lie parallel to the direction of the carbon nanotube. The predicted N 1s energies were calibrated for the LANL2DZ basis set, based on the previously established procedure,⁵⁵ and shifted so that the computational and experimental N 1s energies for the –NH₂ species on the amine-modified substrate line up, in order to show the energy shift upon attachment of the CNTs. This calibration approach has been demonstrated to provide reproducible binding energies for N-containing functional groups to be used for the assessment of surface chemical reactions.^{39,40,56,57}

Time-of-Flight Secondary Ion Mass Spectrometry—The ToF-SIMS analysis was performed on a TOF-SIMS V (ION-TOF, Münster, Germany), equipped with a bismuth primary ion source. The 25 kV Bi₃⁺ primary ion beam was run in high-current bunched mode to the static SIMS limit of 1×10^{12} ions/cm² beam dosage for each spectrum collected. The spectra collected had a mass resolution of $m/m = 9000$ recorded at $m/z = 29$. The Bi₃⁺ primary ions were rastered over an area of $200 \times 200 \mu\text{m}^2$ with a 128×128 pixel density for all spectra. High-resolution negative-ion mode spectra were obtained, but only the most informative regions of the negative-ion mode spectra are presented. The calibration

of the ToF-SIMS data was performed using ION-TOF measurement explorer software (version 6.3). All spectra were calibrated to H^- , H_2^- , C^- , CH^- , CH_2^- , CH_3^- , C_2^- , C_2H^- , C_3^- , C_4^- , C_5^- , C_6^- , and C_7^- . All spectra, except those of the carbon nanotube powders, were further calibrated to the fragment of a single gold atom (Au^-).

RESULTS AND DISCUSSION

To provide a reliable and straightforward method for the covalent bonding of carbon nanotubes to functionalized surfaces directly through the nanotube cage, it is important to confirm that carbon nanotubes are present on a surface following the procedure, that they are deposited at submonolayer coverage, that their binding is covalent, and that the presence of surface functional groups on carbon nanotubes is not needed for this deposition but rather that the binding occurs via chemical reactions of the prefunctionalized substrate surface with the cage of the carbon nanotube directly. To address the first part of the process, microscopy techniques, including SEM, TEM, and AFM, will be applied. The feasibility of a direct covalent link between the substrate and cage of the carbon nanotube will be investigated with DFT computational methods, and to confirm and analyze the covalent binding, XPS and ToF-SIMS will be applied.

Confirmation of Nanotube Presence on the Surface

Dropcasting methods are commonly used to deliver a variety of materials to the surface, and in this work, the same approach is used. However, to remove the multilayers and bundles of nanotubes and to zero in on the nanotubes strongly bound to the surface, sonication is utilized. To confirm that the nanotubes remain on the surface following the sonication process, SEM was used to compare the surfaces before and after this preparation step. Figure 2a,b shows the amine-terminated silicon surface before the addition of CNT-NF. Following the reaction, SEM clearly confirms the presence of the nanotubes, as can be observed in Figure 2c,d. Likewise, the presence of COOH-CNT can be observed on the surface following the deposition and sonication, as demonstrated in Figure 2e,f. Similar results are obtained in Figure 3 for the amine-modified gold surface. It is apparent from the SEM images in Figures 2 and 3 that carbon nanotubes can be deposited on the functionalized surface and that following the sonication process both gold and silicon surfaces retain small but reproducible coverages of both functionalized and nonfunctionalized nanotubes. It also appears that the nature of the substrate does not play a substantial role in the coverage of either functionalized or nonfunctionalized nanotubes following the sonication step. However, SEM does not indicate the type of binding between the nanotubes and the surfaces, and it does not confirm the presence of individual nanotubes or monolayers of nanotubes due to the resolution limit of the instrument. The manufacturer specifications for the diameters of the nanotubes (1–4 nm) suggest that alternative analytical techniques must be used to verify that individual carbon nanotubes are in sufficient enough contact with the surface to interact covalently.

Submonolayer Coverage of Nanotubes on the Functionalized Substrate Surfaces

To verify the expected diameter of the carbon nanotubes, transmission electron microscopy was used. The average diameter of the non-functionalized carbon nanotubes was calculated

to be 1.7 nm from the TEM micrograph shown in Figure 4a, which is consistent with the diameter reported by the manufacturer. Atomic force microscopy was then used to observe the AUD-modified silicon following its reaction with the NF-CNTs and compare it to the AUD-modified silicon surface without introducing nanotubes. Figure 4b shows the flat surface of the amine-terminated silicon whereas Figure 4c,d shows the same surface following its reaction with the CNT. The features present in these micrographs indicate that individual carbon nanotubes can be identified on the surface. Indeed, the height of these features, compared to the manufacturer-reported and TEM-evaluated CNT diameters, confirms that the features correspond to individual carbon nanotubes several hundreds of nanometers in length. The line profile shows that the heights of the CNTs observed in Figure 4d, approximately 1.5 nm, are fully consistent with the sizes of individual nanotubes. It is noteworthy that at a junction where two nanotubes appear to crossover in Figure 4d, the observed height, about 3 nm, is double that of an individual CNT. Thus, an AFM investigation is used to identify individual carbon nanotubes, but more importantly, it demonstrates that these individual CNTs are in intimate contact with the surface. Thus, chemical identification techniques can be used to confirm if this contact is based on covalent binding.

Spectroscopic Evidence of Covalent Binding between Functionalized Surfaces and CNTs

X-ray photoelectron spectroscopy was used to study the surface chemistry of carbon nanotubes on amine-functionalized silicon and gold surfaces. Because the main spectroscopic signature is based on the chemical environment of the nitrogen atom of the functionalized organic layer as it reacts with the carbon nanotubes, Figure 5 compares the XPS results in the N 1s region for the gold and silicon surfaces before and after reaction with the nonfunctionalized carbon nanotubes. It is obvious that the nominally nonfunctionalized carbon nanotubes contain a number of defect sites that are essentially the same as those for the functionalized CNTs, thus in probing the reaction of the NF-CNTs described in this section, it will be important to distinguish the chemical pathways that involved these defect sites from those that could be associated with the reaction directly through the cage of a CNT. The N 1s spectrum in Figure 5b for the AUD-modified silicon substrate shows the main feature at 399.5 eV that represents the majority -NH_2 species and a smaller peak at around 402 eV that is likely an oxidized nitrogen species because the samples were transferred to the XPS under ambient conditions. These assignments are based on previous investigations of amino-terminated organic monolayers^{39,40,56,57} and are in complete agreement with the computational studies presented for the model systems provided in Figure 5, denoted by green lines below the spectra. If this spectrum is compared to that obtained following the reaction with the nonfunctionalized carbon nanotubes (Figure 5a), then the large feature (which now represents a mixture of -NH_2 and -NH- species) shifts the overall binding energy by about 0.5 eV and a smaller peak at around 397.5 appears. The 0.5 eV shift is fully consistent with the formation of the -NH- species by the direct covalent binding of the terminal amine of the organic layer on a substrate surface with the cage of carbon nanotubes by a direct attachment process. This assessment is also supported by the computational investigation of the N 1s shift following such a reaction, as summarized in Figure 5.

The small feature at 397.5 eV could be explained by a side reaction where nitrogen is inserted into an aromatic system of the cage structure (likely at defect sites), and the obtained binding energy is in agreement with previous investigations of similar systems reported in the literature⁵⁸ and with the density functional theory investigations of several model systems summarized in the Supporting Information section. The small peak at around 402 eV is a combination of oxidized nitrogen, and it very likely is covering a feature indicating amide formation due to defects on the carbon nanotubes. However, a direct assignment of this feature is not possible on the basis of these data alone. The system of cysteamine on gold, both before (d) and after (c) reaction with nonfunctionalized carbon nanotubes, shows very similar spectra, with the largest peak at around 399.5 eV shifting up by 0.5 eV following the reaction with the carbon nanotubes and smaller peaks at 397 and 402 eV, which can be similarly assigned to the assignment provided above for the silicon system. The 0.5 eV binding energy shift following amine interactions with the carbon nanotube is in agreement with predicted N 1s core-level energies from density functional theory calculations that were performed separately for the gold and silicon substrate systems. To account for different possibilities of amine attachment to the CNT cage, the positions of the N 1s features were compared for two different types of geometries: one in which the amine dissociates across the bond that is parallel to the CNT and the other in which the amine dissociates across a C=C bond that is not parallel to the direction of the nanotube. The calculated binding energies of these two possible geometries are not identical but are very close to one another. The predicted binding energies are indicated by the green bars underneath the spectra in Figure 5. A complete list of model systems with several different diameters of CNTs is provided in the Supporting Information section. The main conclusions that can be drawn from this set of studies are that the local chemical environment of surface amino groups changes upon the substrate interacting with the carbon nanotubes and that the nature of neither the substrate itself nor the organic linker appears to influence the chemistry of the amino termination with the carbon nanotubes. All of the comparisons provided in Figure 5 are consistent with the reaction of the amino functionality of the surface with carbon nanotubes directly via the attachment through the carbon cage; however, to confirm this, a better understanding of the reaction conditions and specific identification of the surface species produced is needed.

A series of control experiments were performed to confirm the nature of the nitrogen species observed following the surface attachment of carbon nanotubes. First, Figure 5e shows that the nonfunctionalized carbon nanotube powder, analyzed as received, exhibits no features in the N 1s spectral region. Thus, the N 1s features recorded are solely the signatures of the nitrogen species originating from the functionalized surface. To make sure that the reactivity is based on the -NH_2 attachment, the carbon nanotubes were allowed to sonicate with neat propylamine and with propylamine in DMF solvent for 3 h (the same reaction conditions as with the amine-terminated substrates); after being washed to remove unreacted propylamine and solvent, they were dried and analyzed via XPS. The CNTs reacted with neat propylamine (5f) and with propylamine in DMF (5g) show the presence of nitrogen. From the comparison of the peak positions of spectra 5f and 5g with those for amino-functionalized surfaces in Figure 5a,c, it is clear that the reactions result in the formation of similar species in all cases and that this reaction corresponds to the upward shift of the

binding energy of the surface primary amino group. Of course, the differences in intensity and the presence of other features in the surface spectra can be related to the different geometry of interaction, where neat propylamine or propylamine in a solvent would have easy access to all of the functionalities and the entire surface of carbon nanotubes, whereas the substrate amino groups could not possibly react with all potential attachment sites on the carbon nanotubes, and at the same time, the reactivity of the surface could influence the efficiency of the entire process. For example, the carbon nanotube that is efficiently immobilized on an amino-functionalized surface could produce additional linkages via sequential attachment reactions.

Overall, the XPS results suggest four important points: (1) the nitrogen observed in these experiments originates only from the amine-modified silicon and gold substrates and not from impurities in CNTs or from interactions with a solvent, (2) the surface chemistries on the silicon and gold systems are very similar to one another, (3) the interaction between the surface and the carbon nanotubes results in a chemical change, and (4) the spectroscopic signature of the surface species formed is consistent with the direct attachment of surface amino groups to the cage of the carbon nanotubes; however, the nature of this bonding has to be confirmed independently. It should also be pointed out that the C 1s spectral region has also been scrutinized in this work. The resulting spectra are presented in the Supporting Information section; however, because of the presence of the organic monolayer and because of a brief exposure to ambient conditions during sample transfer, the detailed quantitative assignment of all of the observed features is not practical. Nevertheless, there are indeed noticeable changes in the C 1s spectral regions on both gold and silicon surfaces following attachment of the NF-CNTs and the π^* resonance suggests that aromatic structures are deposited in the process, fully consistent with the results of microscopy studies described above.

Confirmation That Attachment through the Cage Is Energetically Feasible

Computational investigations utilizing density functional theory were undertaken to determine whether covalent binding between the CNT cage and modified substrate is possible. Modified substrates (gold and silicon) and (10, 0) carbon nanotubes were modeled and optimized, and the energies of different covalent bonding configurations were computed. CNTs with three different radii (but with identical geometries otherwise) were chosen to compare radius effects on covalent binding to the flat substrate. Two types of binding between the substrate and the cage were considered (and described above): parallel and nonparallel to the longitudinal direction of the CNT. The relative energy (E) of each configuration is compared to its initial optimized components (CNT and the amine-terminated substrate). Figure 6 summarizes these relative energies for the CNTs on gold. The attachment of the smallest-radius CNT is exothermic for the parallel configuration but slightly endothermic for the nonparallel structure. In contrast, the E for the two larger-radius CNTs are endothermic for both geometries, with the smaller E belonging to the nonparallel arrangement. This contrast is likely due to the differences in the radius of curvature and thus in the strain of the resulting adducts. For the smaller-radius CNT, the carbons that make up the π bond that interacts with the substrate amine are not in the same plane and do not greatly interfere with one another. As the radius increases, these carbon atoms in the cage

become more similar to those in a graphene sheet. These relative energies suggest that, whereas some energy input is required to bind the surface to the CNT cage, this interaction is feasible. Very similar results were obtained for calculations on the silicon surface and are summarized in Table S1 of the Supporting Information section, with the differences largely arising from the description of the cluster models for gold and silicon surfaces rather than from the geometrical differences of the structures resulting from the attachment of an amine functional group to the cage of the carbon nanotube. The computational studies suggest that this type of attachment is possible, but in order to experimentally confirm this, further spectroscopic investigation must be performed.

Evidence of Covalent Attachment through the Cage

ToF-SIMS was used to identify specific fragments associated with attachment on the surface. Because of the complex nature of the carbon nanotube system and all of the fragments possible, the assessment of the covalent attachment of carbon nanotubes on the surfaces is very difficult. This is even more complicated in the case of the silicon substrate because of the long carbon AUD chain and the three stable isotopes of silicon. On the other hand, using a gold substrate may simplify the fragment assignments because a single gold isotope provides an excellent marker for such a complex system. At the same time, as described above in the XPS investigation, the attachment chemistry is essentially identical on amino-terminated gold and silicon substrates. Thus, the ToF-SIMS analysis presented below is focused on gold substrates.

Figure 7 shows the ToF-SIMS spectra for the $\text{Au-S-(CH}_2\text{)}_2\text{N}^-$ fragment expected at 270.973006 m/z . The corresponding m/z features are not observed for the carboxylic acid-functionalized or nonfunctionalized carbon nanotubes (Figure 7e,f, respectively), as expected. However, a very prominent peak is observed for the cysteamine-terminated gold (Figure 7d). The same peak is observed for the amino-terminated samples following their reaction with COOH-CNTs and with NF-CNTs (Figure 7a,b, respectively). This is expected because all of the cysteamine-modified gold surfaces should contain this fragment even after their reaction with carbon nanotubes.

A control sample was prepared by modifying a gold substrate with dimethylamino ethanethiol and allowing it to react with the NF-CNTs; this spectrum can be observed in Figure 7c. In this case, the methyl groups on the dimethylamino ethanethiol should protect the amine from chemically interacting with the carbon nanotubes during sonication. The spectrum from this sample also shows a peak for the $\text{Au-S-(CH}_2\text{)}_2\text{N}^-$ fragment, which is expected. This confirms that all of the gold substrates are successfully functionalized with their respective amine-containing molecules.

The spectra in the region of the $\text{A-S-(CH}_2\text{)}_2\text{NH-C}_5^-$ fragment at 331.980830 m/z are summarized in Figure 8 and correspond to cysteamine attached to the substrate and a five-carbon fragment of the carbon nanotube. As expected, no peaks at this m/z position are observed for the carbon nanotube powders (Figure 8e,f) or for the cysteamine-modified gold (Figure 8d). A prominent feature corresponding to this fragment is observed for the cysteamine-terminated gold following its reaction with the carbon nanotubes (Figure 8a,b). By itself, this observation would be insufficient to conclude that the carbon nanotubes are

covalently bound to the surface in this case; however, the control sample with dimethylamino ethanethiol (Figure 8c), which should prevent the covalent bonding of carbon nanotubes to the surface amine group, does not exhibit this feature. This suggests that the five-carbon fragment from the carbon nanotubes is actually bound to the cysteamine through the primary amine.

The next set of experiments explores whether it could be concluded that the binding through the surface amino group requires the participation of the carboxylic acid of the functionalized carbon nanotubes or the participation of the defect sites of the nonfunctionalized carbon nanotube. Figure 9 shows the ToF-SIMS spectra in the region of the $\text{Au-S-(CH}_2)_2\text{N-CO-C}_5^-$ fragment at 358.967921 m/z . This fragmentation is expected to occur when cysteamine interacts with a carboxylic acid to form an amide, such as in the case of the carboxylic acid-functionalized CNTs or with defects on the CNTs. The C_5 portion of the fragment indicates that a five-carbon fragment from the carbon nanotube is attached to the amide. No signal is observed in the spectra for the CNT powders (Figure 9e,f), the cysteamine-modified gold (Figure 9d), or the dimethylamino ethanethiol-modified gold (Figure 9c). Again, this is expected, as the methyl groups on the control sample hinder the reaction between the carbon nanotubes and the amino-functionalized substrate.

In the case of the amino-terminated gold surface reacted with functionalized carbon nanotubes, the attachment through amide formation is expected and has been previously shown to occur with caged structures featuring carboxylic acid.⁴⁰ The main peak in Figure 9a confirms that this is indeed the case. It should, however, be pointed out that the intensity of this feature is very small compared to the peak for the same sample in Figure 8, suggesting that only a part of this reaction occurs through the amide functionality and a substantial portion leads to a direct attachment of the primary amino group to the cage of the carbon nanotube. The ToF-SIMS intensities are only a semiquantitative measure of the extent of reaction, but the previous statement is also reinforced by the relatively small peak from the $\text{Au-S-(CH}_2)_2\text{N-CO-C}_5^-$ fragment for the attachment of nonfunctionalized carbon nanotubes, as shown in Figure 9b, which might occur on the defect sites. An approximation of the percentage of attachment events that occur via the cage versus the carboxylic acid can be determined by comparing the integration of the ToF-SIMS peaks corresponding to the $\text{Au-S-(CH}_2)_2\text{NH-C}_5^-$ and the $\text{Au-S-(CH}_2)_2\text{N-CO-C}_5^-$ fragments. This semiquantitative comparison assumes that the ionization cross sections for the two fragments are similar and indicates that about three-quarters of the COOH-functionalized CNTs attachment takes place through the cage of the nanotube and almost 90% of the nonfunctionalized CNT attachments occur through the cage. Overall, this set of studies implies that the presence of extra functionality is not necessary to covalently bind carbon nanotubes to an amine-terminated surface and that strong, covalent attachment will occur through the cage.

CONCLUSIONS

The covalent attachment of carbon nanotubes to functionalized silicon and gold surfaces has been investigated. Microscopic techniques confirm the presence of flat-lying nanotubes on both substrates and the presence of a sufficient number of nanotubes to allow for covalent binding. Spectroscopic studies suggest that regardless of the presence of functional groups

on carbon nanotubes, they can attach directly through the carbon cage to the amino-functionalized surfaces by a direct addition process. The role of functional groups present on CNTs is important, as they have been shown to react with surface amines; however, the direct attachment through the cage has also been demonstrated to take place, both for functionalized and for nonfunctionalized carbon nanotubes. The experiment with the protected amino functionality of the surface reinforces the role of primary amines as an excellent functional group for attaching carbon nanotubes.

These findings provide a novel approach for the covalent and stable attachment of flat-lying carbon nanotubes to chemically functionalized substrates and to control the architecture of the attachment process, which will be important in many applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Summary of the direct attachment of carbon nanotubes to amine-functionalized silicon and gold surfaces through the CNT cage.

Figure 2. SEM micrographs of the amine-modified silicon surface before (a) and after reaction with NF-CNT (c) and COOH-CNT (e). (b, d, and f) Close-up views of the surface before the reaction and following the reaction with NF-CNT and COOH-CNT, respectively.

Figure 3. SEM micrographs of the amine-modified gold surface before (a) and after reaction with NF-CNT (c) and COOH-CNT (e). (b, d, and f) Close-up views of the surface before reaction and following the reaction with NF-CNT and COOH-CNT, respectively.

Figure 4.

TEM (a) confirmation of carbon nanotube diameter, which is in agreement with the manufacturer's specification. AFM micrographs of (b) the AUD-modified silicon surface and (c, d) the AUD-modified silicon surface following the reaction with NF-CNTs. The line profile of the white line in d shows the height of the CNTs.

Figure 5.

XPS investigation of the N 1s spectral region of the AUD-modified silicon surface before (b) and after (a) reaction with the NFCNTs and the cysteamine-modified gold surface before (d) and after (c) reaction with the NF-CNTs. Spectra of control experiments compare (e) NF-CNT powder, (f) NF-CNT reacted with neat propylamine, and (g) NF-CNT reacted with propylamine in DMF. The green bars underneath the spectra indicate the expected binding energies for selected systems, predicted by density functional theory calculations. The presence of two DFT-predicted binding energies below spectra a and c indicate the expected values for the N 1s energies in a geometry in which the amine dissociates across a C=C bond parallel to the direction of the CNT and one in which the amine dissociates across a C=C bond that is not parallel to the direction of the CNT.

Figure 6. Relative energies of parallel and nonparallel (denoted in red and blue) attachment configurations on cysteamine-modified gold surfaces for CNTs with radii of different sizes.

Figure 7.

ToF-SIMS spectra in the region of the $\text{Au-S-(CH}_2\text{)}_2\text{N}^-$ fragment, which is indicative of the successful modification of the substrate with cystamine or dimethylamino ethanethiol. Features are absent in the case of the carbon nanotube powders (e, f) but can be observed for this peak on the cystamine-terminated gold before (d) and after reaction with both the COOH-CNTs and NF-CNTs (a, b) and on the dimethylamino ethanethiol-terminated gold (c). The black bar below the spectra indicates the exact m/z position expected for the fragment.

Figure 8.

ToF-SIMS spectra in the region of the $\text{Au-S-(CH}_2\text{)}_2\text{NH-C}_5^-$ fragment, which is indicative of cysteamine bound to the substrate and to a five-carbon fragment of a carbon nanotube. Features are absent in the case of the samples without the substrate (e, f), on the cysteamine-terminated gold before reaction (d), and the control sample (c) but can be observed after reaction with both the COOH-CNTs and NF-CNTs (a, b). The black bar below the spectra indicates the exact m/z position expected for the fragment.

Figure 9.

ToF-SIMS spectra in the region of the $\text{Au-S-(CH}_2)_2\text{N-CO-C}_5^-$ fragment, which is indicative of amide formation resulting from carboxylic acid (attached to a five-carbon fragment) reacting with the primary amine of cysteamine. These features are absent in the case of the samples without the substrate (e, f), the modified gold surface (d), and the control sample (c). A small peak can be observed on the cysteamine-terminated gold after reaction with the NF-CNTs (b), and a large peak is observed on the amine-modified gold after reaction with the COOH-CNTs (a). The black bar below the spectra indicates the exact m/z position expected for the fragment.