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Functionalization of carbon nanotube AFM probes using tip-activated gases

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Abstract

Multiwalled carbon nanotube (MWNT) probe microscopy tips have been functionalized with gases, activated in a transient arc produced at the tip ends. Adhesion measurements between these tips and hydroxyl-terminated monolayers versus pH reveal that MWNT tips reacted in O_2, H_2 and N_2 display acidic, pH-independent and basic properties, respectively. MWNT tips derivatized in O_2/N_2 and H_2/N_2 mixtures demonstrate the greater reactivity of carbon nanotubes towards O_2 and H_2, respectively. Moreover, the chemical reactivity of tips functionalized in N_2 suggests termination in aromatic nitrogen heterocycles. Tip-activated gas functionalization of MWNTs provides facile generation of chemically sensitive nanoprobes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

A significant advance in atomic force microscopy [1–3] (AFM) has been the development of carbon nanotube tips [4–8]. The high aspect ratio of carbon nanotubes allows them to probe, for example, deep crevices and trench structures [4]. The smaller effective radii compared to conventional tips, which in the case of single-walled nanotubes (SWNTs) can be as small as 0.5 nm, permit improved resolution in the imaging of biomolecules [5] and nanostructures [6]. In addition, the ability of carbon nanotubes to buckle elastically [9] limits the force applied by the AFM probe, which can reduce deformation and damage to soft biological and organic samples, while at the same time making these probes exceedingly robust.

An ideal high-resolution probe should also be accessible to chemical modification to enable molecular-scale sensing and manipulation of matter. We have recently demonstrated that both MWNT [7] and SWNT [8] tips can be covalently-modified using carbodiimide coupling chemistry to create a wide-range of tip functionality. These derivatized nanotube probes allow detection of unbinding events between individual ligand–receptor pairs, such as biotin and streptavidin [7], as well as chemically-sensitive imaging of patterned samples with a functional group resolution as small as 3 nm [8].

The basis for our previous functionalization of MWNT and SWNT probes is that the oxidized ends of nanotubes terminate with carboxyl groups (COOH). This termination is consistent with previous data on oxidized graphite [10,11] and bulk oxidized nanotubes [12], and was confirmed by direct

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force titrations [7,8]. While selective covalent coupling to the terminal COOH groups permits attachment of a wide range of functional groups, the solution phase reactions required for this chemistry are often difficult to complete without mechanically damaging the probes. In this latter regard, we have been exploring alternative methods of modifying carbon nanotube probes, that can (i) be carried out in a single step and (ii) produce a range of functionality at the tip ends. Herein, we demonstrate that carbon nanotubes can be functionalized using O_2, H_2, and N_2 after activation with a momentary arc created at the tip end. The tips functionalized in this simple one-step procedure exhibit predictable acidic, pH-independent, and basic behavior using air/O_2, H_2, and N_2 gases, respectively.

2. Experimental

All AFM experiments were carried out with a Multimode Nanoscope III (Digital Instruments, Santa

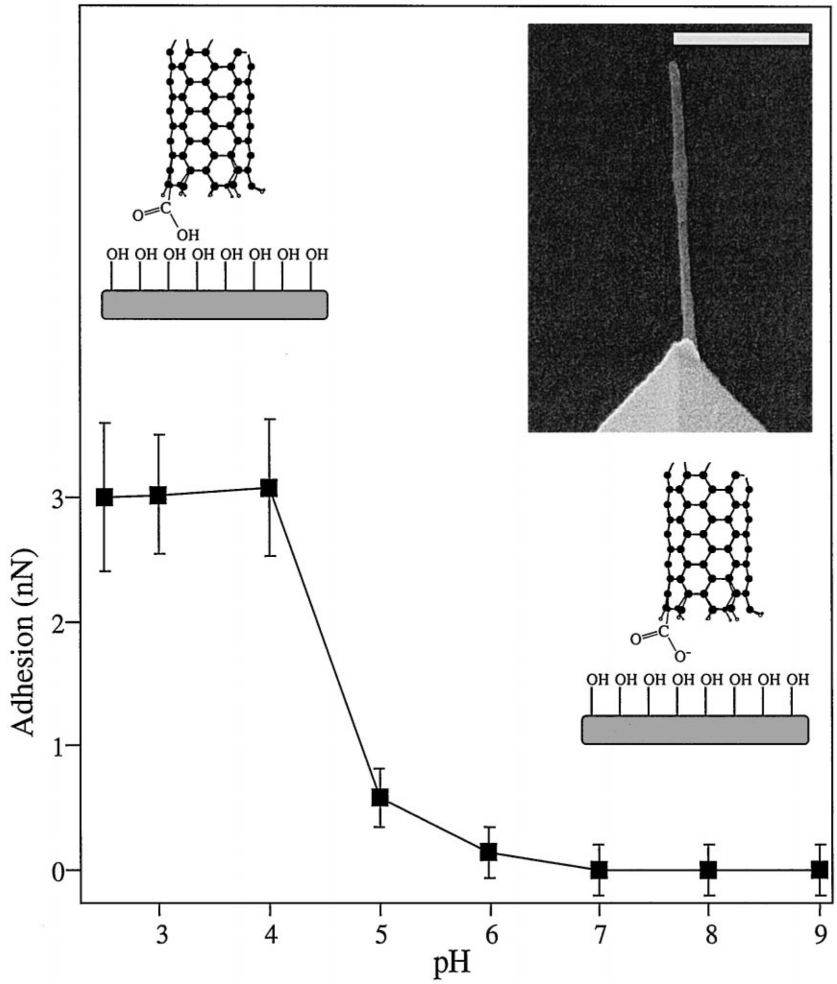

Fig. 1. Adhesion as a function of pH between a MWNT tip modified in air/O_2 and an OH terminated SAM. Each data point corresponds to the mean of 50–100 adhesion measurements and the error bars represent one standard deviation. The schematics illustrate qualitatively the ionization state and the interaction measured at low and high pH. (inset) Scanning electron microscopy image of a shortened MWNT tip. The scale bar is 1 μm.

Barbara, CA). MWNT samples were purified by oxidation (700°C, air) until ~2% of the original mass remained [13]. MWNT probes were prepared as described previously [4,5] by using an acrylic adhesive to affix a MWNT bundle onto the pyramid of a Au coated force modulation etched silicon probe (FESP) tip (Digital Instruments) under the direct view of an optical microscope in dark-field illumination. Since the mounted MWNTs are generally too long and wide for high-resolution imaging, the length and radius of each MWNT tip was optimized by applying a bias voltage (0.5–20 V) between the tip and a sputtered Nb surface (Nioprobe, Electron Microscopy Services, Fort Washington, PA) in a gaseous environment; the applied voltage produces a momentary discharge during the optimization process. Tips were shortened in air as described previously [4,5] and were reacted in other gases by flowing N_2, H_2 or a 1:1–1:2 mixture of N_2/H_2 at a rate of 50–300 ml/min through the AFM fluid cell while a bias was applied between the tip and the Nb surface. As a precaution, the H_2 was mixed with excess N_2 and safely exhausted after exiting the fluid cell.

To assess the functionality at ends of MWNT tips, we performed force titrations [14,15] that involve measuring the pH dependence of the adhesion force between tips and a non-ionizable hydroxyl-terminated (OH) self-assembled monolayer (SAM) formed on a flat Au(111) surface [7,8]. The –OH terminated SAMs were prepared by immersing Au-coated Si samples into a 2–3 mM ethanolic solution of 11-mercaptoundecanol for at least 12 h. All SAMs were rinsed in ethanol and dried in a stream of nitrogen prior to use. Buffered 10 mM phosphate solutions were used to vary the pH for the titrations. All force titrations were repeated several times using different tips to ensure reproducibility. We attempted to further functionalize several N_2 sharpened MWNT tips by allowing them to react in a solution of 50 mM EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (Pierce, Rockford, IL) and 5 mM sodium benzoate (Mallinckrodt, St. Louis, MO) in 0.1 M MES (2-[*N*-morpholino]ethanesulfonic acid) (Sigma, St. Louis, MO) buffer pH 6.0, for 2 h. These tips were then successively washed in 0.1 M solutions of MES, NaCl (Fisher, Pittsburgh, PA), and deionized water prior to performing force titrations.

3. Results and discussion

Our group has previously demonstrated that adhesion measurements as a function of pH made between functionalized silicon nitride [14,15] or nanotube tips [7,8] and substrates functionalized with SAMs terminating in non-ionizable OH groups, are sensitive to the ionization state of the chemical groups at the tip end. Fig. 1 shows the result of a force

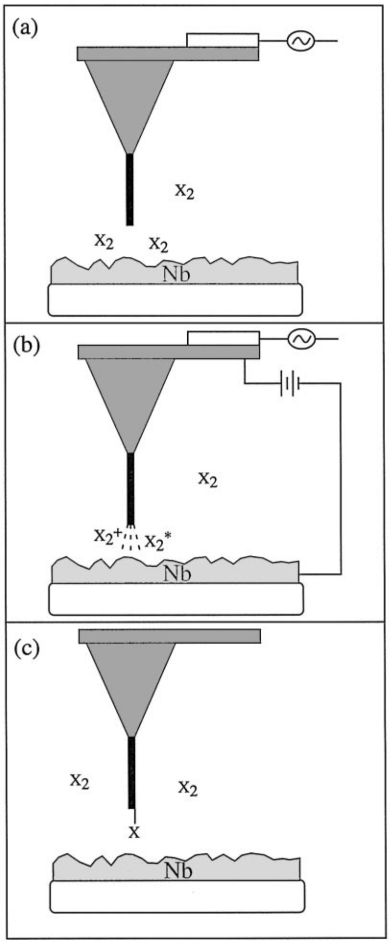

Fig. 2. Schematic of carbon nanotube functionalization process. (a) Carbon nanotube (heavy, black vertical line) attached to a Si cantilever is oscillated near resonance above a sputtered Nb surface in the presence of gas, X_2. (b) A potential applied between the oscillating cantilever/nanotube assembly and sputtered Nb substrate produces a discharge that activates surrounding gas molecules (X_2^+, X_2^*). (c) Subsequent reaction at the nanotube tip produces a tip functionalized with 'X'. In these studies, X corresponds to O, H, or N.

titration between a MWNT tip, which was sharpened in air, and an OH-terminated SAM surface. The adhesion is finite (~ 3 nN) at low pH values and drops off sharply at pH ~ 4.5 with no measurable interaction at higher pH. This pH dependence of adhesion is indicative of the presence of COOH groups at the tip; at low pH these are protonated and have a finite interaction with the OH surface, while at high pH, they are deprotonated and no interaction is detected [7,8,14,15].

These force titration results and subsequent chemical reactions [7,8] show that COOH groups do exist at the ends of the carbon nanotube tips that have been shortened in air using the electrical process. We can understand at least qualitatively the formation of the COOH groups as follows (Fig. 2). The potential applied between the oscillating cantilever/nanotube tip and Nb surface produces a momentary arc discharge. In this discharge, two things occur. First, carbon is removed from the nanotube end in a process believed to be assisted by high electric fields [16]. This process creates reactive carbon sites at the tube end. Second, the discharge can activate, through field and electron impact ionization, the surrounding gas molecules. In the cases of H_2, N_2, and O_2, ionized (e.g., H_2^+, N_2^+, and O_2^+, respectively), excited state and atomic species can be produced [17,18]. More specifically, we suggest that the activated oxygen reacts at nanotube ends to form the observed carboxyl groups.

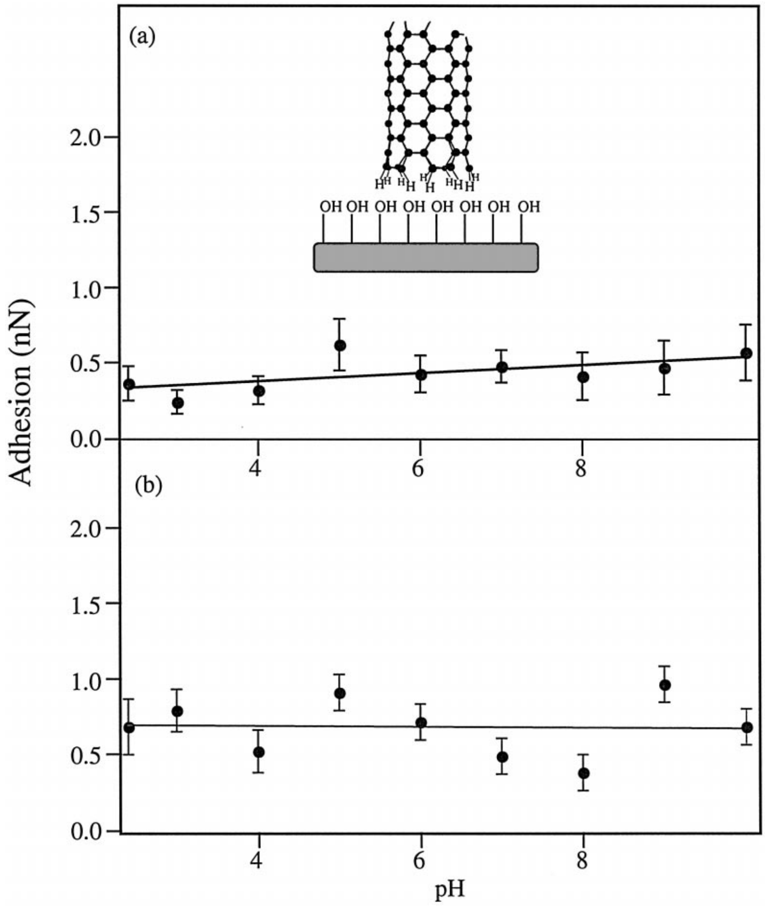

Fig. 3. (a) Adhesion as a function of pH between a MWNT tip which was modified in H_2, and an OH terminated SAM. Each data point corresponds to the mean of 50–100 adhesion measurements and the error bars represent one standard deviation. The schematic illustrates the proposed H-termination of the nanotube. (b) Data recorded on an independent MWNT tip modified in H_2.

This scenario for the activation of oxygen and the formation of carboxyl groups suggests that it may be possible to create other functionality at the tip ends by activating different gases with the discharge. To explore this proposal, we have investigated the use of the momentary discharge to activate H_2, N_2, and H_2/N_2 mixtures for nanotube functionalization. Fig. 3 details the adhesion as a function of pH between a MWNT tip modified in H_2 and an OH-terminated SAM surface. Here the interaction force between the

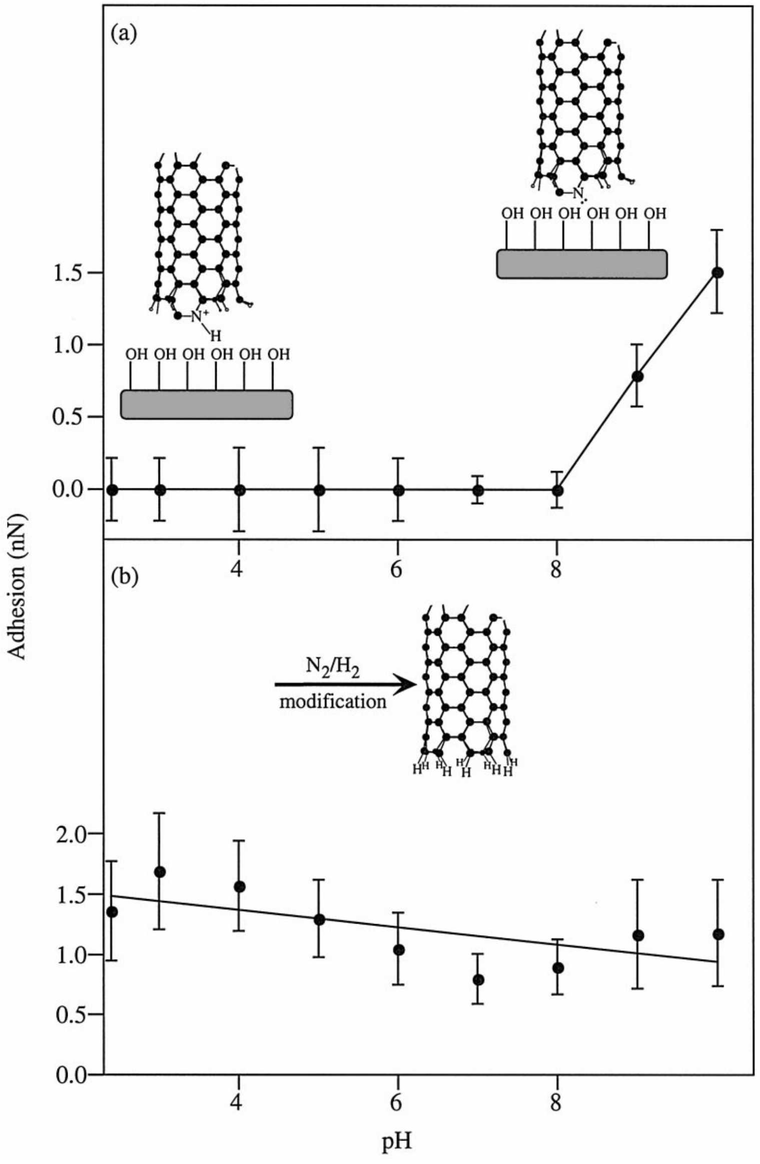

Fig. 4. (a) Adhesion as a function of pH between a MWNT tip modified in nitrogen and an OH terminated SAM. Each data point corresponds to the mean of 50–100 adhesion measurements and the error bars represent one standard deviation. The schematics illustrate qualitatively the ionization state and interaction measured at low and high pH. (b) Adhesion as a function of pH between a MWNT tip modified in a N_2/H_2 mixture and an OH-terminated SAM. The schematic illustrates the preferential termination of the nanotube with hydrogen.

tip and substrate is finite (~ 0.5 nN) and displays little dependence on pH. This result demonstrates the formation of non-ionizable functionality at the tip end, and is clearly distinct from that observed for tips modified in air. The pH-independent behavior is consistent with a nanotube tip terminating in hydrogen. We also find that modification in activated hydrogen yields reproducible pH-independent behavior (Fig. 3b), and thus we believe that modification using hydrogen represents a reliable method for producing non-ionizable nanotube probe tips.

In addition, we have investigated the modification of nanotube tips using activated N_2. Significantly, force titrations recorded with these modified tips exhibit pH-dependent behavior with no measurable force at low pH and finite adhesion at $pH > 8$ (Fig. 4). This pH-dependent behavior shows that MWNT tips modified in N_2 have basic functionality at their ends. In an effort to characterize further the nature of the nitrogen base at the ends of these tips, we studied their reactivity. In particular, well-defined carbodiimide chemistry [19] was used in an attempt to couple benzoic acid to the ends. If the coupling were successful, force titrations would exhibit a pH-independent response. The requirement for a successful coupling reaction is the presence of a primary or secondary amine to react with COOH. Notably, we find these coupling reactions, which were very successful for COOH-terminated tips and primary amines [7,8], did not modify the strongly pH-dependent behavior of the tips (e.g. Fig. 4a). These experiments show that the basic nitrogen is not a primary or a secondary amine. Based on the known graphitic structure of MWNTs (sp^2 hybridized carbon) and these experimental results, we hypothesize that the terminal functional groups are basic aromatic nitrogen heterocycles. Additional reactivity studies will be needed in the future to test this hypothesis.

Lastly, we have studied the competitive functionalization of nanotube tips in the presence of activated N_2/H_2 (Fig. 4b). Our motivation for these experiments was to assess whether it would be possible to create primary or secondary amine groups at the nanotube ends. Force titration data recorded with MWNT tips modified in 1:1 to 1:2 N_2/H_2 mixtures showed, however, pH-independent behavior similar to that obtained in pure H_2. These results suggest that the tips are H-terminated and that under these experimental conditions H_2 is significantly more reactive than N_2 and hence determines the resulting tip functionality.

4. Conclusions

We have demonstrated that MWNT AFM tips can be selectively functionalized by a momentary arc discharge from the tip end in different gases. MWNT tips modified in this way in air yield terminal COOH functionality. Tips modified in H_2 terminate in inert, pH-independent groups, whereas tips modified in N_2 end in basic nitrogen functionality. The ability to create acidic, basic, and pH-independent carbon nanotube probes this way represents a straightforward method for making different types of well-defined functionalized tips without requiring additional chemical derivatization, for example, through solution chemistry. In addition, it may be possible to exploit our approach in conjunction with different gases to elaborate further the chemical functionality at the ends of nanotubes. More generally, these functionalized carbon nanotube probes offer the potential for chemically sensitive imaging of materials, nanostructures and biomolecules at the nanometer scale. Such nanotips should be sensitive to specific intermolecular interactions important to chemistry and biology, and should prove useful for mapping chemically distinct domains of self-assembled polymeric and biological materials.

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