*J. Am. Chem. Soc.* **1996,** *118,* 6303−6304

# Electrochemically Controlled Adhesion in Atomic Force Spectroscopy

James E. Hudson and Hèctor D. Abruña*

*Department of Chemistry, Baker Laboratory*
*Cornell University, Ithaca, New York 14853-1301*

*Received November 20, 1995*
*Revised Manuscript Received February 20, 1996*

It has been recently demonstrated that atomic force microscopy (AFM), in addition to providing topographic information, can also be a powerful tool for investigating surface chemistry and adhesion by modifying the AFM tip to induce and/or enhance specific interactions between tip and sample. Modified tips have been employed to both map chemical functionality on a sample surface by measuring the friction between tip and sample in a lateral force microscope[1] and directly measure the adhesion force between two species using force spectroscopy.[1,2] The ability to manipulate the chemical properties of an AFM tip to tune the function of AFM is an exciting advance with wide ranging applications.

We report here the first study of adhesion between electroactive polymer films immobilized onto electrode surfaces using an AFM operated in the force mode. Unique to this system, as we will show, is the ability to control the degree of adhesion through the selective oxidation or reduction of the polymer films. The ability to control adhesion in this manner could prove useful in a variety of applications including the design of new microscopies which will be sensitive to multiple surface interactions.

A schematic of the experimental apparatus is shown in Figure 1A. A gold foil and a gold-coated AFM tip[3] were modified with an approximately 35 nm thick film[4] of poly(vinylferrocene) (PVF) by electrochemical deposition from a methylene chloride solution according to previously described procedures.[5] Tips were characterized by scanning electron microscopy (SEM) using a Leica 440 microscope operated at 20 kV. Comparison of SEM images of gold-coated tips before (Figure 1B) and after (Figure 1C) modification with PVF shows that the polymer film is evenly spread across the electroactive regions of the tip. However, due to the difficulty of imaging PVF by SEM,[6] the radius of curvature at the contact region of the tip is unknown.

Force spectroscopy measurements were performed in a glass fluid cell using a Nanoscope III multimode microscope (Digital Instruments, Santa Barbara, CA). The tip, contacted through an uninsulated metal clip, and the foil were grounded together and kept under potential control in a 0.10 M aqueous $KClO_4$ electrolyte solution using a BAS CV-27 potentiostat (Bioanalytical Systems, West Lafayette, IN) interfaced to the AFM. A polished silver wire was used as a quasi reference electrode, and a large area platinum coil was used as a counter electrode.

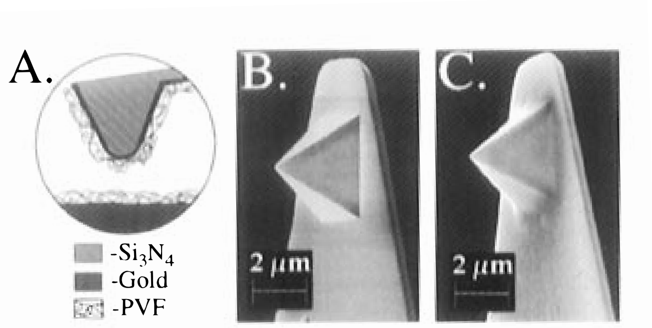

**Figure 1.** (A) Schematic representation of a gold substrate and gold-coated AFM tip, modified with a thin film of poly(vinylferrocene) (PVF). The tip and film were mounted inside a glass fluid cell in an atomic force microscope and held under potential control. (B) SEM image of a clean, gold-coated AFM tip. (C) SEM image of a gold-coated AFM tip modified with a 35 nm thick film of PVF.

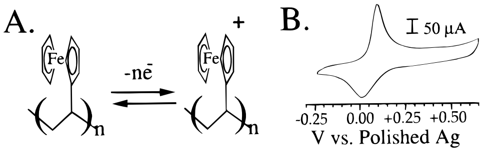

**Figure 2.** (A) Reaction scheme for oxidation of PVF to $PVF^{n+}$. (B) Cyclic voltammogram of the tip and sample taken in the fluid cell in 0.1 M $KClO_4$ at a scan rate of 50 mV/s.

Cyclic voltammetry taken in the AFM fluid cell of the PVF-modified AFM tip and foil (Figure 2B) shows the characteristic reversible oxidation at $E = +0.05$ V vs polished silver corresponding to the one-electron oxidation of each ferrocene subunit (Figure 2A). Force spectroscopy measurements were then performed while holding the potential of the tip and substrate either negative or positive of the PVF oxidation wave corresponding to the neutral and oxidized forms of the polymer, respectively.

In force spectroscopy, the deflection of an AFM tip is measured as a sample is moved into and then out of contact with the tip. The characteristic hysteresis observed when the sample is retracted is due to adhesion between the tip and sample. The point at which the adhesion is broken and the AFM tip pulls off the surface is characterized by a sharp discontinuity in the force plot. The magnitude of this discontinuity provides a direct measure of the adhesion force between the tip and the sample with near piconewton resolution.

Characteristic force curves measuring the interaction between neutral polymer films ($E = -0.25$ V vs polished silver) and the interaction between oxidized polymer films ($E = +0.30$ V vs polished silver) are shown in parts A and B of Figure 3, respectively. In all experiments, the maximum applied contact forces were minimized, to avoid destroying the pliable polymer films. Statistical analysis of over 100 consecutive force curves for each type (plotted as a histogram fitted by a Gaussian distribution) yields an average adhesion force of 12.2 ± 0.3 nN for the neutral polymer films and 3.2 ± 0.4 nN for the oxidized polymer films.[7] These results could be consistently repeated without changing the tip or substrate, suggesting that the polymer films do not deteriorate through repeated scanning.

Though likely the result of many factors, we ascribe the large difference in adhesion force as primarily due to differences in solvation energies.[8] The decrease in hydrophobicity upon

---

[1] (a) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, *265*, 2071−2073. (b) Noy, A.; Frisbie, C. D.; Rozsnyai, L. F.; Wrighton, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 7943−7951. (c) Green, J.-B. D.; McDermott, M. T.; Porter, M. D. *J. Phys. Chem.* **1995**, *99*, 10960−10965.

[2] (a) Rabinovich, Y. I.; Yoon., R.-H. *Langmuir* **1994**, *10*, 1903−1909. (b) Florin, E. L.; Moy, V. T.; Gaub, H. E. *Science* **1995**, *264*, 415−417. (c) Lee, G. U.; Chrisey, L. A.; Colton, R. J. *Science* **1994**, *266*, 771−773.

[3] Commercially available silicon nitride AFM tips (Digital Instruments, Santa Barbara, CA) were coated by thermal evaporation of a 25 Å chromium adhesion layer followed by a 500 Å layer of gold in vacuum ($5 \times 10^{-7}$ Torr).

[4] Film thicknesses were estimated by integrating the charge under the cyclic voltammetric wave corresponding to the oxidation of the ferrocene centers of a PVF film deposited onto a planar electrode of known area for the same time and conditions as that of the tip and substrate.

[5] (a) Roullier, L.; Waldner, E. J. *Electroanal. Chem.* **1985**, *187*, 97−107. (b) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3222.

[6] Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *112*, 97−115.

[7] Adhesion force calculations assume a force constant of 0.06 N/m, the published value for an unmodified, commercially available cantilever (Digital Instruments). The actual force constant of the modified tip is likely larger than the assumed value; therefore, emphasis is placed on the relative magnitudes of the adhesion forces.

[8] (a) Ducker, W. A. *Langmuir* **1992**, *8*, 1831−1836. (b) Hoh, J. H.; Cleveland, J. P.; Prater, C. B.; Revel, J.-P.; Hansma, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 4917−4918.

S0002-7863(95)03876-5 CCC: $12.00

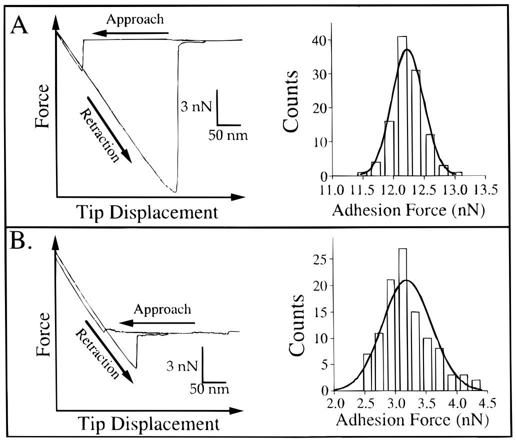

**Figure 3.** Typical force curves and histograms showing the number of times a given force was observed (fitted by a Gaussian distribution) for (A) interactions between neutral polymer films ($E = -0.25$ V vs polished silver) and (B) interactions between oxidized polymer films ($E = +0.30$ V vs polished silver).

oxidation of PVF films is well-known. Willman and Murray[9] studied the contact angle between a drop of aqueous electrolyte and a PVF film and reported a contact angle of 78° for the neutral film and 63° for the oxidized film. The surface of the neutral polymer is hydrophobic, and since force experiments were performed in an aqueous electrolyte, the hydrophobicity of the polymer surface should strongly influence the adhesion force. Conversely, the oxidized form of the polymer is much less hydrophobic, incorporating solvent and electrolyte into its structure to maintain charge balance. The decrease in hydrophobicity significantly reduces the adhesion between the polymer films. It is notable that at these electrolyte concentrations, electrostatic interactions will be almost entirely screened but may contribute slightly to the decrease in adhesion.[10] However, charge screening by the electrolyte should also minimize any electrostatic repulsion between the gold electrode surfaces, thereby ensuring that the observed decrease in adhesion is dominated by the interaction of the polymer films. A more thorough study of electrostatic interactions at lower electrolyte concentrations will be presented in future work.

Control of the AFM tip's surface chemistry also enables a ready means of probing multiple chemical interactions with a single tip. For example, a PVF modified tip can be electrochemically switched between sensitivity to solvaphilic surfaces and sensitivity to solvaphobic surfaces in polar solvents. In Figure 4 are presented typical force curves for the interaction of oxidized and neutral PVF films with functionalized surfaces terminating in either carboxylate groups (A, C) or less wettable methylene groups[11] (B, D) in an electrolyte of 0.05 M KOH in ethanol.[12] Qualitatively, the magnitudes of the observed adhesion forces suggest that the oxidized polymer interacts more strongly with carboxylate than the methylene while the neutral polymer interacts more strongly with methylene than with carboxylate. It is therefore possible to monitor both solvaphobic and solvaphilic interactions using the same AFM tip without disengaging the microscope. While it is possible to tailor two different tips to have these properties,[1] changing tips in AFM is both time consuming and makes it difficult, if at all possible, to return to the same region of the sample surface.

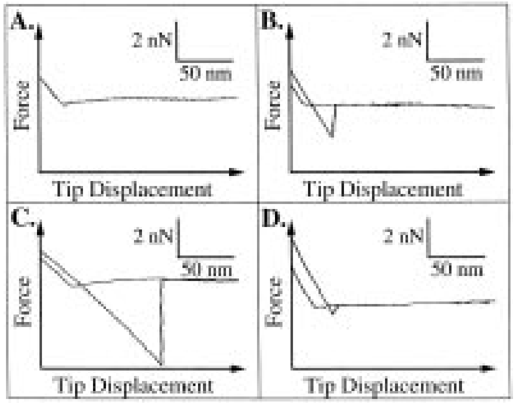

**Figure 4.** Typical force curves for the interactions of a neutral PVF film ($E = -0.25$ V vs polished silver) with (A) a carboxylate-terminated surface and (B) a methylene-terminated surface and typical forces curves for the interactions of an oxidized PVF film ($E = +0.30$ V vs polished silver) with (C) a carboxylate-terminated surface and (D) a methylene-terminated surface.

We have demonstrated the first electrochemically controlled adhesion in an atomic force microscope and have demonstrated a unique application. The ability to remotely control the surface chemistry of an AFM tip, as we have done, adds an exciting new dimension to scanning probe microscopy. Future work will focus on the effects of electrolyte concentration and the use of an electrochemically controlled tip in the design of a novel mechanical switch, as a versatile lateral force microscopy probe and as a tool for repositioning molecular adsorbates.

**Acknowledgment.** This work was supported by the Office of Naval Research (AASERT Program) and the National Science Foundation (Grant No. DMR-9107116). We are grateful to the Material Science Center at Cornell University for the use of their AFM and SEM facilities. J.E.H. acknowledges support by a Department of Education Fellowship and an NSF training grant.

JA953876S

---

(9) Willman, K. W.; Murray, R. W. *Anal. Chem.* **1983**, *55*, 1139−1142.

(10) (a) Butt, H. J. *Biophys. J.* **1991**, *60*, 777−785. (b) Butt, H. J. *Biophys. J.* **1991**, *60*, 1438−1444. (c) Senden, T. J.; Drummond, C. J.; Kékicheff, P. *Langmuir* **1994**, *10*, 358−362. (d)Lin, X.-Y.; Creuzet, F.; Arribart, H. *J. Phys. Chem.* **1993**, *97*, 7272−7276.

(11) Abbott, N. L.; Gorman, C. B.; Whitesides. G. M. *Langmuir* **1995**, *11*, 16−18.

(12) Carboxylate-terminated surfaces and methylene-terminated surfaces were prepared by immersing clean gold samples for 1 h in 5 mM solutions of 3-mercaptopropanoic acid and 1-hexanethiol in ethanol, respectively. Samples were thoroughly rinsed with ethanol and 0.05 M ethanolic KOH solution.