Redox Activation of a Polyaniline-Coated Cantilever: An Electro-Driven Microdevice**

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The integration of chemical activity with micromechanical force sensors has opened up fundamentally new approaches for the development of novel microdevices. While the atomic force microscopy (AFM) lever is a sensitive spring that undergoes mechanical bending and acts as a force sensor, the coupled chemical component may be used to activate the forces on the cantilever. The AFM optical detection system can be used as a sensitive detector for the cantilever movement or deflection as a result of forces exerted by the chemical element on the cantilever. With the development of micromechanical sensors over the past decade, it is now possible to measure forces below 1 pN (10^{-12} N). The advantages of using cantilever sensors lies in their dimensions: typically several hundred microns long and 0.5 to 1 μm thick. These miniature dimensions give rise to small spring constants (typically 0.1–10 $\mathrm{N\,m^{-1}}$) and high resonance frequencies (10 kHz–1 MHz) which translate to high sensitivity and fast response times. The use of AFM cantilevers as sensors has already been demonstrated in various applications.[1–3] Temperature, power, and surface-energy changes of 10^{-5} K, 10 pW, and 20 fJ, respectively, were detected with a bimetallic-strip coated cantilever.[4] Mass changes occurring on the cantilever,[5] down to 1 pg, measurement of the surface stress associated with an electrochemically deposited metal monolayer on the cantilever,[6, 7] and the determination of binding energies[8] enable the characterization of chemical reactions by force responses of the modified cantilevers. Recently, force interactions on cantilevers were employed to characterize protein binding[9] and particularly the specific DNA hybridization[10] on a cantilever surface.

In all of the described systems, the principle is that the cantilever will deflect when subjected to a force or moment. In systems where surface stress in layers adsorbed on one side of the cantilever exert the force on the cantilever, one may use the Stoney's formula [Eq. (1)] to relate the cantilever deflection to changes in the surface stress, where $\Delta\sigma$ is the stress difference between the two sides of the cantilever, ΔZ is the deflection of the free-end of the cantilever, L is the length, t is the thickness, E is Young's modulus, and v is the Poisson ratio of the cantilever.

$$\Delta\sigma = \frac{Et^2}{3(1-v)L^2}\Delta Z \qquad (1)$$

Here we report the development of an electro-driven micromachine by the electrochemical deposition of polyaniline[11, 12] on one side of the cantilever. Upon oxidation of the polymer, the cantilever is subjected to stress, a result of the electrostatic repulsion of the polymer chains and of a polymer swelling process that results in the deflection of the cantilever. Reduction of the oxidized polymer will release the stress and the cantilever will retract to its original position.

By the cyclic oxidation and reduction of the polymer, the cantilever is reversibly deflected from and restored to the original position, respectively. We are able to monitor the kinetics of swelling and shrinking of the polymer film by following the time-dependent deflection of the cantilever.

The electrochemical liquid cell depicted in Figure 1 consists of an Au-coated cantilever, a gold wire, and a silver wire which operate as a working electrode (WE), a counter electrode (CE), and a quasi-reference electrode (RE), respectively. The cantilevers employed in our experiments are commercially available triangular Si_3N_4 AFM cantilevers coated on one side with approximately 40 nm of Au. The cantilevers have a length of 160 μm and a thickness of 0.6 μm. Using Equation (1) we find that for these levers a deflection of the end of the lever by 1 nm (10^{-9} m) corresponds to a surface stress of 1.7 $\mathrm{N\,m^{-1}}$. Given that the sensitivity of the deflection sensor is approximately 0.1 nm, then a practical limit for surface-stress measurements in liquids is about 0.2 $\mathrm{N\,m^{-1}}$. The Au-coated cantilevers were cleaned by sonication in acetone then in isopropanol and rinsed with deionized water. The cantilevers were then subjected to a plasma etch (50:50 O_2:Ar) to remove any residual contaminants. Electropolymerization of aniline on the Au surface of the cantilever was performed in a 0.1 M

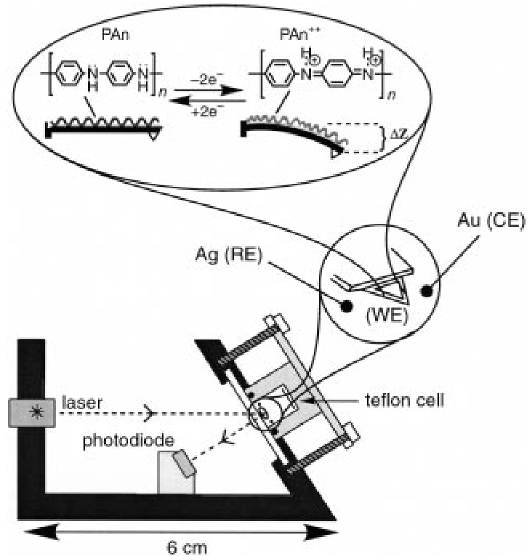

Figure 1. The system used for in situ electrochemically induced stress measurements on the cantilever. Inset shows the reversible electrochemical oxidation–reduction of the polyaniline film and the resulting lever deflection, see text for full details.

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H_2SO_4/0.5 M Na_2SO_4 solution in the presence of the aniline monomer (0.1 M) upon the application of a constant potential, $E = 0.8$ V versus the Ag-quasi-reference electrode. Electrolysis was conducted for 10 seconds. By coulometric assay of the charge passed through the cell, and knowing the Au-surface area, the average thickness of the polyaniline (PAn) film was estimated to be 190 nm. This value is in excellent agreement with the estimated thickness of the PAn film prepared by a similar method, and measured using surface plasmon resonance spectroscopy.[13a]

The PAn-functionalized cantilever was subjected to a multipotential-step chronoamperometric experiment in a mixture of 0.1 M H_2SO_4/0.5 M Na_2SO_4. The potential steps from −0.2 V to 0.8 V result in an electrochemically induced transition from the reduced polymer state, PAn, to the oxidized polymer state, PAn^{2+}, whereas the potential steps from 0.8 V to −0.2 V result in the polymer reduction ($PAn^{2+} \rightarrow PAn$). Figure 2 A shows the chronoamperometric responses of the polymer film upon application of the potential steps that result in the oxidation and the reduction of the PAn film with a 50 second gap between the potential steps. Figure 2 B shows the respective time-dependent stress on the cantilever resulting from the electrochemical oxidation–reduction process of the polymer. The stress values were calculated using Equation (1) from the experimental deflection signal measured simultaneously with chronoamperometric responses. It is evident that upon oxidation of the PAn film, the cantilever is deflected, which implies the development of stress on the lever. The reduction of the polymer releases the stress and the lever is restored to its original rest position. The stress on the lever and the concomitant deflection, are reversibly stimulated by the cyclic multistep potential changes resulting in the electrochemical oxidation and reduction of the polymer film. Control experiments reveal that a bare Au-covered cantilever is not deflected upon performance of the similar multistep chronoamperometric experiment. Also, the application of the same potential step sequence on the PAn-modified cantilevers in 0.1 M phosphate buffer (pH = 7.0), conditions where the PAn is redox inactive, does not yield any stress (or deflection) on the lever. These results indicate that the oxidation and subsequent reduction of the polymer film control the cyclic stress exerted on the cantilevers upon the application of the multistep potential sequence on the electrode. Close examination of the stress developed on the lever (Figure 2 B) reveals that upon oxidation of the polymer to the PAn^{2+} state, an instantaneous increase in the stress on the lever is observed to approximately 2.3 $N m^{-1}$ followed by a time-dependent increase in the stress to about 3.9 $N m^{-1}$ after approximately 50 seconds. The rapid increase in the stress on the lever is attributed to electrostatic repulsion between the oxidized, positively charged polymer chains. The slow increase in stress on the lever is attributed to swelling of the PAn^{2+} film. The swelling and shrinking of polyaniline films on electrode supports resulting from redox-transformations is well established.[13] In a recent study[13a] employing surface plasmon resonance (SPR) spectroscopy, we demonstrated that the oxidation of a PAn film to PAn^{2+} is accompanied by a swelling process exhibiting a rate constant of $k_{sw} = (3.0 \pm 0.3) \times 10^{-4}\ s^{-1}$. Kinetic analysis of the time-dependent stress changes on the lever reveals that this is a first-order process with a rate constant corresponding to $k' = (2.8 \pm 0.3) \times 10^{-4}\ s^{-1}$, very similar to the swelling rate constant observed by SPR. Similarly, the retraction of the lever to its original position upon the reduction of the film ($PAn^{2+} \rightarrow PAn$) reveals an instantaneous release of the stress, followed by a substantially slower time-dependent decrease in the stress, Figure 2 B. Our SPR study has revealed that reduction of the PAn^{2+} polymer is accompanied by shrinking, $k_{sh} = (5.0 \pm 0.5) \times 10^{-4}\ s^{-1}$. Kinetic analysis of the time-dependent stress release on the lever upon the reduction of PAn^{2+} to PAn reveals that it is a first-order process, $k'' = (6.0 \pm 0.5) \times 10^{-4}\ s^{-1}$, very similar to the rate of shrinking of the reduced polymer. Thus, the stress induced on the levers upon oxidation of the polymer film to the PAn^{2+} state is attributed to electrostatic repulsions between charged polymer chains, and to the swelling of the polymer film as a result of its oxidation. The detailed kinetic analysis of the slow deflection and retraction processes of the lever are provided as Supporting Information.

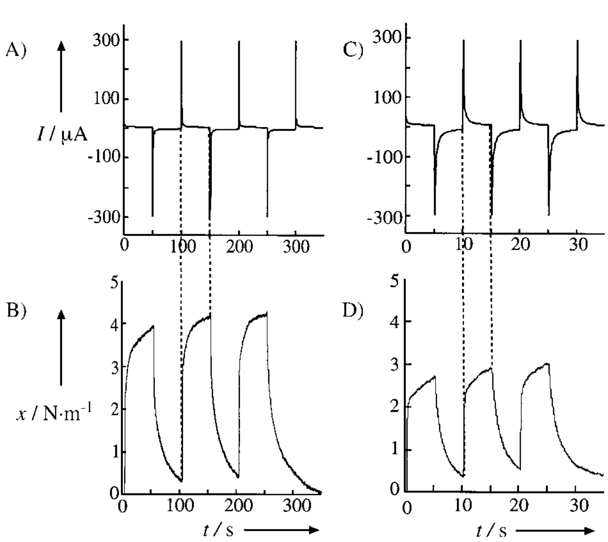

Figure 2. A) Chronoamperometric transients measured upon the multistep potential changes from −0.2 V to 0.8 V and from 0.8 V to −0.2 V with the time-gap of 50 s. B) Time-dependent cantilever stress generated upon the potential changes shown in (A). C) Chronoamperometric transients measured upon multistep potential changes from −0.2 V to 0.8 V and from 0.8 V to −0.2 V with the time-gap of 5 s. D) Time-dependent cantilever stress generated upon the potential changes shown in (C). The experiments were performed in a 0.1 M H_2SO_4/0.5 M Na_2SO_4 solution; anodic current is positive; (x = surface stress).

Figures 2 A and C show the transient-current responses of the PAn-modified cantilever upon application of the multistep potential changes using different intervals between the steps. Integration of the resulting current responses, indicates that the charge associated with the oxidation of PAn to PAn^{2+} is independent of the oxidation–reduction time width, which suggests that the PAn^{2+} content is similar in both systems. Figures 2 B and D show the cyclic stress responses of the cantilever subjected to the multipotential pulses of different time widths. The immediate stress developed on the polymer-functionalized lever upon application of the 5 s potential-pulse gap, around 2.3 N m^{-1}, is almost identical to the instantaneous stress developed on the lever upon the application of the 50 s potential pulse gap. This is consistent with the electrostatic repulsive interactions in the two polymer films being similar because of identical surface coverage of the oxidized polymer. The stress on the polymer subjected to the 50 s potential step continues to increase with time as a result of the swelling process, whereas the swell-induced stress on the polymer-functionalized lever, on which the 5 s potential-step is applied, is prohibited.

The chronoamperometric transients observed upon the oxidation (or reduction) of the polymer (cf. Figure 2 C), reveal, however, that the oxidation (or reduction) of the polymer film proceeds in about 5 s. Thus, further shortening of the potential-step time interval is anticipated to lead to incomplete oxidation of the polymer and to a decrease in the yield of the PAn^{2+} product. This would yield lower repulsive interactions and lower stress on the lever as the time interval of the potential step decreases. Figure 3 shows that the surface stress on the lever decreases, as the potential-step pulse is shorter. At pulse widths shorter than 10 ms no deflection of the lever is observed, which implies that the response-time of the electrochemically driven microdevice is $\tau = 10$ ms.

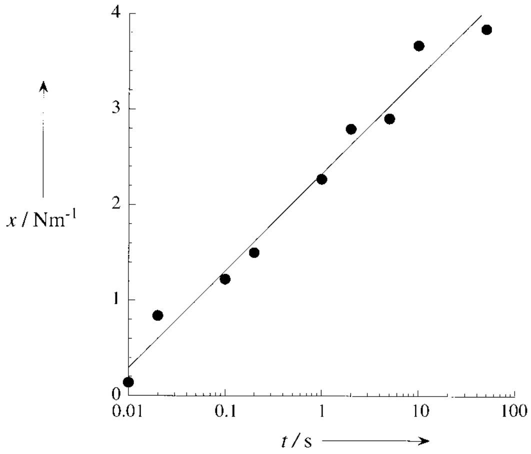

Figure 3. Saturated cantilever stress value as a function of the time between the potential steps. The potential steps from -0.2 V to 0.8 V and from 0.8 V to -0.2 V were applied on the polyaniline-modified cantilever immersed in a 0.1 M H_2SO_4/0.5 M Na_2SO_4 solution; (x = surface stress).

In conclusion, we have designed an electrically driven micromachine where a polyaniline-functionalized cantilever is reversibly deflected and returned to a rest position as a result of cyclic potential steps. The degree of lever deflection (or stress) is controlled by the electrostatic repulsive interactions in the polymer and the swelling of the film. One may envisage such electropowered levers as microactuators, micropumps, or microrobotic elements. As different other stimuli such as light,[14] thermal,[15] or chemical,[16] may induce the swelling of polymer films, the tailoring of other signal-triggered microdevices is envisaged. The method presented here complements recent activities to fabricate microactuators[17] and microrobots.[18] With all these signal-triggered devices, new functional sensors, biosensors, and "smart" micromachine devices are envisaged.[19]

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