

ENVIRONMENTAL MONITORING USING MICROCANTILEVER SENSORS

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Introduction

There is presently an urgent need for rugged, low cost sensing systems for real-time, in-situ chemical, physical, and radiological sensors in the characterization and monitoring of mixed waste, ground water, contaminated soil and process streams. Miniature sensors will have applications ranging from plume containment and remediation to determination of location, chemical composition, and level of Dense Non-Aqueous Phase Liquids (DNAPLs). The emergence of mass-produced microcantilevers promises to bring about a revolution in environmental sensing applications [1-3]. Preliminary results show that microcantilever sensors have sensitivity in the range of sub parts-per-billion for operation even under solution conditions. Molecular adsorption on cantilever surface results in cantilever bending when the adsorption is confined to a single surface. The motion of the cantilever can be sensitively detected using a number of techniques such as optical beam deflection, changes in piezoresistivity, piezoelectricity, capacitance, and tunneling current.

However, microcantilever sensors do not offer any chemical selectivity. Chemical selectivity is achieved by using selective coatings applied to one side of the cantilever. Cantilevers can be coated with self-assembled monolayers with chemical recognition head groups for molecular recognition. Consequently, it becomes apparent that microcantilevers are a universal platform upon which to base a multitude of electro-mechanical sensors for measuring physical, chemical, and even biochemical factors, depending upon the selection of the coating.

Materials and Methods

We used commercially available silicon microcantilevers (Park Instrument, CA) in these experiments. The dimensions of the V-shaped microcantilevers are 200 μm length, 20 μm width, and 1 μm thickness. One side of the cantilever is vacuum deposited with a 40 nm thick layer of gold using e-beam evaporation. . Chemical selectivity is achieved by using self-assembled monolayers (SAM) coupled with molecular recognition agents. The deflection measurements were carried out with an AFM apparatus (Digital Instruments). The cantilever surfaces were modified using selective self-assembled monolayers. To demonstrate cantilever operation under solution, we have detected a number of ions such as Cs^+ and CrO_4^{-2} . The experiments were performed in a glass fluid cell that holds the V-shaped microcantilever. The volume of the glass cell was 0.2 cm^3 , ensuring a fast replacement of the solution.

Microcantilever deflection changes as a function of adsorbate coverage when adsorption is confined to a single side of a cantilever (or when there is differential adsorption on

opposite sides of the cantilever). Using Stoney's formula and equations of bending of a cantilever, a relation can be derived between the cantilever bending and changes in surface stress. Since we do not know the absolute value of the initial surface stress, we can only measure the variation in surface stress. The surface stress variation between top and bottom surface of a cantilever can be written as [4]:

$$\Delta\sigma_1 - \Delta\sigma_2 = \frac{zEt^2}{4L^2(1-\nu)} \quad (1)$$

where, z is the cantilever deflection, E is the Young's modulus, L is the cantilever length, t is the thickness and ν is the poisson ratio. Since all the quantities on the right hand side can be measured (or known *a priori*), the changes in surface stress due to adsorption can be calculated.

Results and Discussion

We have successfully detected Cs^+ ions in a flowing solution using an ion-selective SAM coated microcantilever capable of detecting cesium ions in the presence of high concentrations of potassium or sodium ions. Our data shows that the sensitivity of this cantilever-based sensor for in-situ measurements is several orders of magnitude better than the currently available using ion selective electrodes (ISEs).

The cesium selective molecular recognition agent used in this work was 1,3-alternate 25,27-bis(11-mercapto-1-undecanoxy)-26,28-calix[4]benzocrown-6, (**1**), bound to a gold-coated microcantilever. The crown cavity of 1,3-alternate conformation of calix[4]benzocrown-6 has been shown to be very selective cesium ions with Cs/Na and Cs/K selectivity ratios in excess of 10^4 and 10^2 respectively, determined using a solvent extraction technique. Binding constant values of 10 , 2×10^4 , and 2.5×10^6 have also been determined by a fluorescence technique for Na^+ , K^+ , and Cs^+ in solution. Based on the high selectivity exhibited by these compounds, receptor molecules can be designed and anchored onto the cantilever surface with a 25 nm coating of gold evaporated on one side. The selectivity of this molecular recognition agent is due to a combination of the correct hole size of the crown ether portion and the rigidity imparted by the calixarene framework (pre-organization). Figure 3 shows the response of this SAM coated cantilevers to Cs^+ ion concentration. The most dramatic response is exhibited when the concentration of cesium is in the range 10^{-7} - 10^{-11} M. In contrast, the cantilever response to potassium ions (the most prevalent interfering ion) in the same concentration range is very small.

The bending response of the SAM coated microcantilever upon Cs^+ , K^+ and Na^+ exposure was also compared for the same concentration of each ion (10^{-5} M). The result indicated that the SAM coated microcantilever was much more selective towards Cs^+ ions compared to K^+ and Na^+ ions. In fact, Na^+ ions have a minimal effect (if any) on the bending response while K^+ ions exhibit enough sensitivity to interfere (as a perturbing ion when present) in the detection of cesium ions.

We have also demonstrated that microcantilevers, modified by a self-assembled monolayer of triethyl-12-mercaptododecylammonium bromide, can be used to detect nanomolar concentrations of CrO_4^{2-} in aqueous solution [5]. Cr(VI) is particularly toxic, and our ability to detect this species is superior to the sensitivity achieved by ISEs. The triethyl-12-mercaptododecylammonium modified cantilever bends up toward the gold side of cantilever upon sorption of CrO_4^{2-} . The sorption of CrO_4^{2-} ions at the surface in place of singly charged anions requires the involvement of two quaternary ammonium molecules to maintain electrical neutrality. Thus the layer bends “up” in response to the change in surface stress caused by the selective ion exchange process.

Our investigations show that metal ions such as Cs^+ and CrO_4^{2-} can be detected using modified microcantilevers. The sensitivity of detection of Cs^+ and CrO_4^{2-} using a surface modified cantilever is much higher than the ISE method. These results provide further evidence that an ion-selective SAM coated cantilever can be applied successfully to the detection of trace amounts of ions in solution. This new concept can be applied to the detection of various ions for environment remediation and monitoring applications as well as biomedical assays. Experiments are presently underway on sensors for other ions using cantilevers modified by different molecular recognition materials. The design and fabrication of a multi-element sensor array device based on cantilever elements specifically modified for the detection of specific ions is apparent.

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