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Detection of CrO_4^{2-} Using a Hydrogel Swelling Microcantilever Sensor

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Hydrogels containing various mounts of tetraalkylammonium salts were used to modify microcantilevers for measurements of the concentration of CrO_4^{2-} in aqueous solutions. These microcantilevers undergo bending deflection upon exposure to solutions containing various CrO_4^{2-} concentrations as a result of swelling or shrinking of the hydrogels. The microcantilever deflection as a function of the concentration of CrO_4^{2-} ions is nearly linear in most concentration ranges. It was found that a concentration of 10^{-11} M CrO_4^{2-} can be detected using this technology in a fluid cell. Other ions, such as Br^- , HPO_4^{2-} , and NO_3^- , have minimal effect on the deflection of this cantilever. The anions SO_4^{2-} and CO_3^{2-} could interfere with the CrO_4^{2-} detection, but only at high concentrations ($>10^{-5}$ M). Such hydrogel-coated microcantilevers could potentially be used to prepare microcantilever-based chemical and biological sensors when molecular recognition agents are immobilized in the hydrogel.

Microcantilevers provide an outstanding platform for chemical and biological sensors because they have excellent dynamic response in a small package, with the opportunity to have integration of micromechanical components with on-chip electronic circuitry.^{1–12} One unique characteristic of microcantilevers

is their ability to undergo bending due to molecular adsorption or binding-induced change in surface tension. This is achieved by confining the adsorption to one side of the cantilever.^{6–8} Microcantilever bending occurs in both air and solution. The key to microcantilever sensor development is to choose appropriate coatings for identification of chemically specific species. Two approaches have been used to immobilize the molecular recognition agents to the microcantilever surface. In the first approach, self-assembled monolayers have been proven successful for the detection of species in water,^{2–5} while in the second, polymeric films, such as those developed for surface acoustic wave (SAW) devices, have been used for detection in the gas phase.^{6,7} Recently, a polymer-coated microcantilever was also developed for measuring pH in solution.⁸

Chromium exists in the environment in different oxidation states in the groundwater, seawater, and soil.¹³ Cr(VI) in the form CrO_4^{2-} is stable in neutral and alkaline environments, and it has been found to be very toxic to animals and humans.¹⁴ Accordingly, the development of methods for the detection of CrO_4^{2-} in the environment is extremely important. Recently, we reported a CrO_4^{2-} sensor based on a microcantilever modified with a self-assembled monolayer of a triethyl-12-mercaptopdodecylammonium salt.⁵ The surface-modified microcantilever sensor selectively responded to CrO_4^{2-} with minimum interference from other anions, including Cl^- , CO_3^{2-} , and SO_4^{2-} , etc. The detection limit of this sensor to CrO_4^{2-} was 10^{-9} M; however, the sensor gradually lost its sensitivity over one week because of the instability of the monolayer. Thus, the design of other coatings for the microcantilever is required for long-term monitoring purpose.

Stimuli–response hydrogels change volume in response to small changes in ionic strength,¹⁵ solvent,¹⁶ stress,¹⁷ light intensity,¹⁸ electric field,¹⁹ and magnetic fields.²⁰ Such behavior has led

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to efforts to develop chemical and biological sensors for species such as glucose,²¹ Pb^{2+} ,²² etc. The sensor platforms investigated to date include electrode,²³ fluorescence,²⁴ and crystalline colloidal array reflection.²⁵ Taking advantages of the volume-changeable property of the hydrogel, we report here a hydrogel-coated microcantilever sensor for the detection of CrO_4^{2-} . (3-Acrylamidopropyl)-trimethylammonium chloride (ATAC) was polymerized in a cross-linked hydrogel network as a result of its ability to form an ion pair with the CrO_4^{2-} anion following ion exchange from aqueous solution.

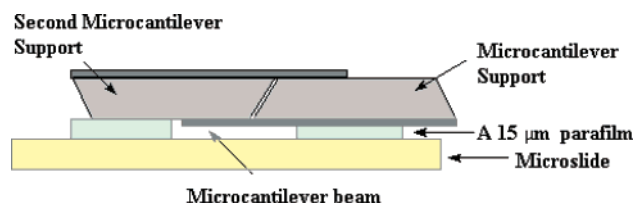
METHODS

1. Solvent and Materials. We used commercially available silicon microcantilevers (Veeco Instruments, CA) in all of our experiments. The dimensions of the V-shaped microcantilevers were $180\ \mu\text{m}$ in length, $25\ \mu\text{m}$ in leg width, and $1\ \mu\text{m}$ in thickness. One side of the cantilever was covered with a thin film of chromium (3 nm) followed by a 20-nm layer of gold, both deposited by e-beam evaporation. The other side of the microcantilever was silicon with a thin naturally grown oxide layer.

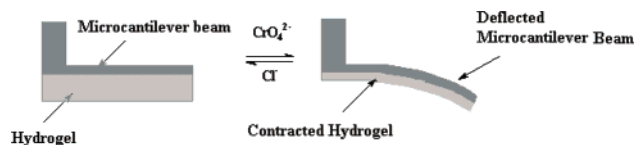
The chemicals used in these experiments, including Na_2CrO_4 , NaCl, NaBr, Na_2CO_3 , NaHPO_4 , NaNO_3 , allytriethoxysilane (ATS), MeOH, EtOH, (3-acrylamidopropyl)trimethylammonium chloride (ATAC), acrylamide (AMD), the cross-linker *N,N'*-methylene-bis(acrylamide) (bis-AMD), and the UV photoinitiator diethoxyacetophenone (DEAP), were used as received from Aldrich. High-purity deionized water was obtained with a Milli-Q water system (Millipore). The pH of the deionized water was 6.82. The pH of a $10^{-3}\ \text{M}$ solution of NaCl was 7.0. The CrO_4^{2-} , Br^- , HPO_4^{2-} , NO_3^- , CO_3^{2-} , and SO_4^{2-} solutions used in our microcantilever deflection experiments were prepared in a $10^{-3}\ \text{M}$ solution of NaCl. The pH of all these solutions was 7.0.

2. Polymerization Procedure. The precursor solution contained 2.1 mmol of AMD, 0.06 mmol of ATAC, 0.072 mmol of bis-AMD, and 0.0072 mmol of DEAP dissolved in 3 mL of water. A microcantilever was placed on a $1\ \text{cm}^2$ quartz microslide, separated from the quartz by a $15\text{-}\mu\text{m}$ Parafilm spacer. The microcantilever support was placed on the Parafilm spacer above the quartz surface so that there was a $15\text{-}\mu\text{m}$ distance between the microcantilever beam and the quartz microslide. The top and bottom sides of the microcantilever beams were gold and silicon surfaces, respectively. To prevent the exposure of the gold-coated surface to the solution, a second microcantilever was positioned to cover the gold-coated side of the first cantilever (Scheme 1). The quartz microslide was placed in the bottom of a vial that contained a precursor solution. The vial was cooled in an ice bath and then exposed to UV light from a 254-nm mercury lamp to initiate polymerization. After 12 min of exposure, the vial was removed

Scheme 1



Scheme 2



from the UV light and the ice bath. The attachment of the hydrogel to the microcantilever silicon surface was observed by high-resolution optical microscopy. No hydrogel was attached on the gold surface, as observed using a microscope. The resulting hydrogel film bound to the substrate was exchanged and equilibrated in a $10^{-3}\ \text{M}$ solution of NaCl for 1 day.

3. Deflection Measurement. The deflection experiments were performed in a flow-through glass cell (Digital Instruments, CA) such as that used in atomic force microscopy. The V-shape microcantilever was immersed in a $10^{-3}\ \text{M}$ NaCl electrolyte solution. Initially, the NaCl solution was circulated through the cell using a syringe pump. A schematic diagram of the apparatus used in this study was previously reported.⁵ Since a change in the flow rate induces noise in the cantilever bending signal due to turbulence, a constant flow rate of 4 mL/h was maintained during the entire experiment. Experimental solutions containing the base electrolyte and the anions of interest were injected directly into the slowly flowing fluid stream via a low-pressure injection port/sample loop arrangement. This arrangement allowed for continuous exposure of the cantilever to the desired solution without disturbing the flow cell or changing the flow rate. Since the volume of the glass cell, including the tubing, was only 0.3 mL, a relatively fast replacement of the liquid in contact with the cantilever was achieved.

Microcantilever deflection measurements by the optical beam deflection method were carried out with an AFM photodiode. The bending of the cantilever was measured by monitoring the position of a laser beam reflected from the cantilever onto a four-quadrant photodiode. The cantilever was immersed in the electrolyte solution until a stable baseline was obtained and the voltage of the position-sensitive detector was set as background corresponding to 0 nm. In our experiment, we define "bending down" as cantilever bending toward the silicon side while, "bending up" refers to bending toward the gold side.

RESULTS AND DISCUSSION

A $15\text{-}\mu\text{m}$ -thick layer of an ATAC copolymerized gel, coated on the surface of a microcantilever, was initially exposed to a constant flow (4 mL/h) of a $10^{-3}\ \text{M}$ solution of NaCl. When solutions containing various concentrations of CrO_4^{2-} solutions were injected into the fluid cell, the microcantilever bent toward the gel side (silicon side) with different amplitudes as shown in Figure 1a. The microcantilever deflection increased as the concentration

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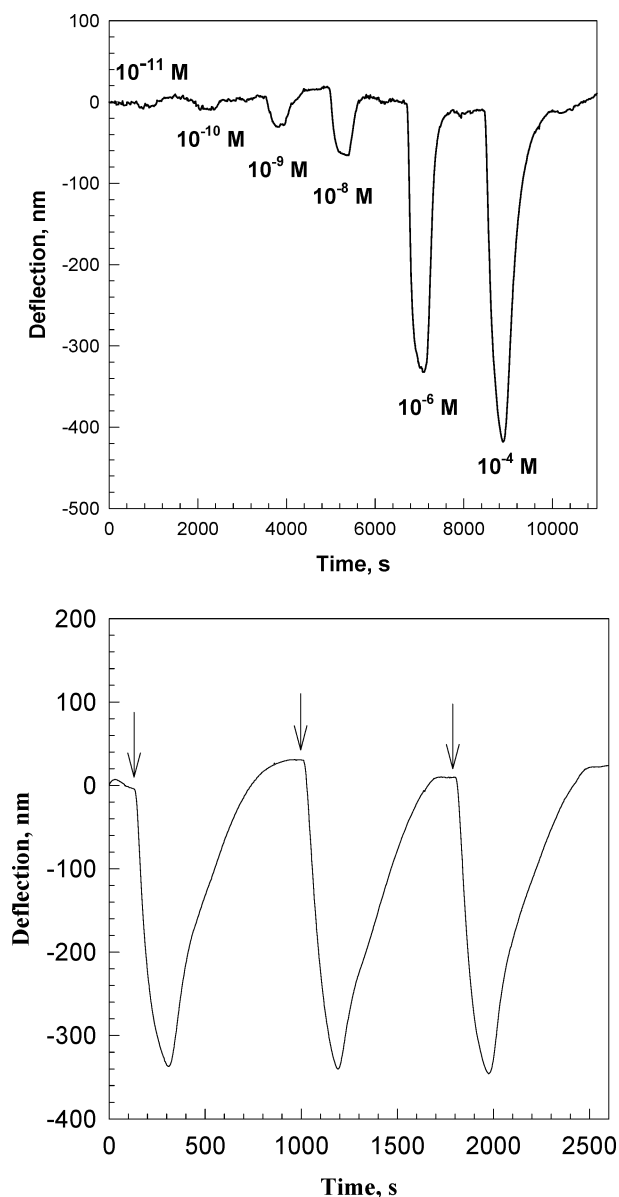


Figure 1. (a) Bending response as a function of time for a silicon microcantilever coated with a 15- μm -thick layer of ATAC copolymerized hydrogel coated upon injection of different concentrations of CrO_4^{2-} solutions in 0.001 M NaCl background electrolyte solution. (b) Three replications of the bending response as a function of time following injection of a solution of 10^{-6} M CrO_4^{2-} in 0.001 M NaCl solution (the injection point is indicated with arrows). Silicon microcantilever coated with a 15- μm -thick ATAC copolymerized hydrogel.

of CrO_4^{2-} increased. For each measurement, a 0.5-mL aliquot of CrO_4^{2-} solution in 10^{-3} M of NaCl was switched into the fluid cell, where the microcantilever was held. It took 7.5 min for the injected CrO_4^{2-} solution in 10^{-3} M NaCl to flow through the fluid cell, and at this time, the original 10^{-3} M NaCl solution was circulated back into the fluid cell. This correlates well with our observations that the deflection of the microcantilever reached a maximum ~ 7.5 min after the injection of various CrO_4^{2-} solutions. After this point, the microcantilever deflection gradually returned to its original position as the solution composition returned to the original 10^{-3} M NaCl solution.

Repeated exposure of the same 10^{-5} M solution of CrO_4^{2-} to the same cantilever modified with the hydrogel caused similar

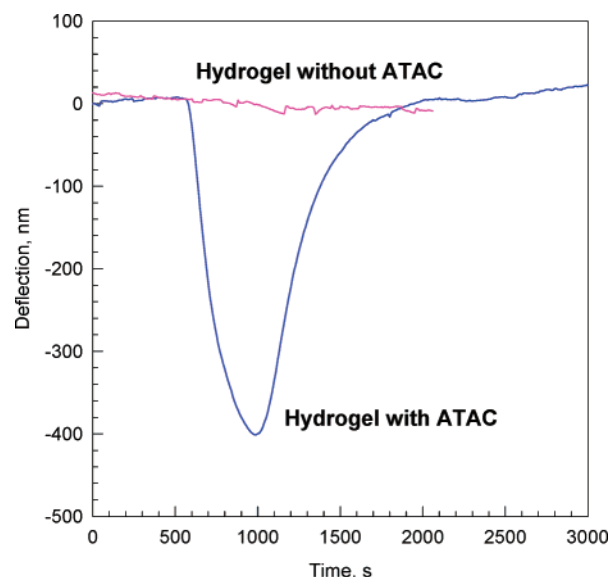


Figure 2. Bending response as a function of time, t , for silicon microcantilevers coated with hydrogel with and without ATAC component on the gold surface after injection of a solution of 10^{-4} M CrO_4^{2-} in 0.001 M NaCl. The microcantilevers were preequilibrated in the 0.001 M NaCl solution before injection of the CrO_4^{2-} solution.

deflection amplitudes and bending rates, as shown in Figure 1b. The standard error is within 5%, indicating good measurement-to-measurement reproducibility.

Control experiments were performed with an unmodified microcantilever and using a microcantilever coated with a 15- μm -thick hydrogel without the ATAC component. No deflection of the cantilever was observed upon exposure to a 10^{-4} M solution of CrO_4^{2-} , as shown in Figure 2. Hydrogel film stability experiments were conducted on a microcantilever coated by an ATAC copolymerized hydrogel after 1 month and 2 months of storage in a 0.001 M NaCl solution. The cantilever deflection showed a similar profile and bending amplitude as those in Figure 2. This is a significant improvement in stability, as compared to the self-assembled monolayer-based microcantilever CrO_4^{2-} sensor that had been previously developed.⁵

Figure 3 is a plot of the maximum deflection amplitude of a microcantilever coated with a tetraalkylammonium-containing hydrogel versus the concentration of CrO_4^{2-} . The plot shows that this microcantilever can be used for the detection of CrO_4^{2-} with a concentration as low as 10^{-11} M in a solution with NaCl background electrolyte. The maximum bending of the microcantilever upon exposure to CrO_4^{2-} was ~ 400 nm. The effects of other anions, such as Br^- , HPO_4^{2-} , NO_3^- , SO_4^{2-} , and CO_3^{2-} , on the deflections of the cantilever are also shown in Figure 3. Br^- , NO_3^- and HPO_4^{2-} , SO_4^{2-} and CO_3^{2-} showed no effect on the cantilever when the concentrations of these anions were below 10^{-6} M. At higher concentrations, NO_3^- , HPO_4^{2-} , and SO_4^{2-} caused moderate cantilever deflections. The deflection at 10^{-4} M was 110, 280, and 510 nm for NO_3^- , HPO_4^{2-} , and SO_4^{2-} , respectively. An ~ 700 -nm deflection of the cantilever was observed when a 10^{-4} M concentration of CO_3^{2-} interacted with the hydrogel on the microcantilever.

Each point shown on the curve for CrO_4^{2-} represents the mean $\pm \text{SE}$ from three independent determinations. The error induced

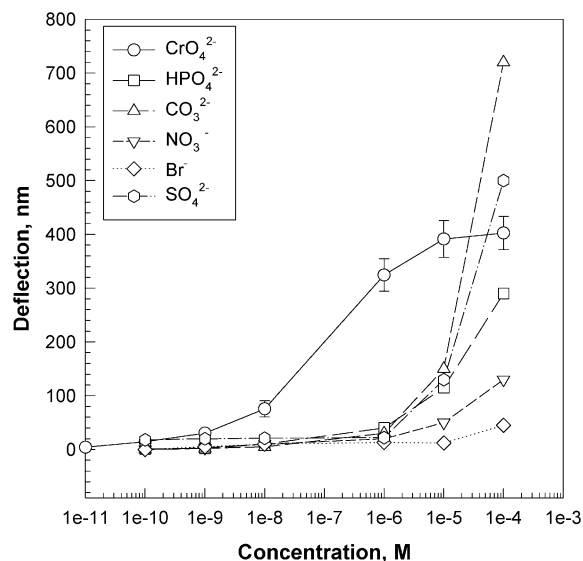
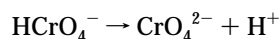


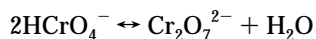
Figure 3. Maximum bending amplitude for a microcantilever coated with ATAC copolymerized hydrogel as a function of the change in concentration of CrO_4^{2-} and other anions.

by different microcantilevers was found to be within $\pm 10\%$. The data shows reasonably good reproducibility from cantilever to cantilever.

The results given above indicate that the hydrogel swells or shrinks upon ion exchange of CrO_4^{2-} or one of the other anions for Cl^- . The predominant Cr(VI) species under the experimental conditions of our experiments is CrO_4^{2-} . From the reported equilibrium constants for protonation of the chromate anion, extrapolated to infinite dilution,



The measured $\text{p}K_a$ is 6.5 (25 °C),²⁶ showing that the dianion predominates at pH 7. The pH-dependent dimerization equilibrium for chromate dianion,



has $\log K$ of 1.52 (25 °C, infinite dilution),²⁶ also confirming that at the concentrations under consideration in this work ($< 10^{-4}$ M), the chromate dianion predominates.

The expansion and contraction of gels allow chemical or electrical energy to be converted into mechanical work. Composite hydrogels have been well-studied over the past 30 years. We will adopt the standard hydrogel swelling theories elaborated by Flory^{27a} and Tanaka^{27b} to explain the volume change of the hydrogel upon exposure to CrO_4^{2-} . Recently, the hydrogel swelling upon interaction of specific analyte with receptors fixed to the hydrogel polymers has been intensively studied by Asher.²⁸

In these theories, the equilibrium hydrogel volume is determined by the summation of three energies,

$$\Delta G_{\text{tot}} = \Delta G_{\text{mix}} + \Delta G_{\text{elas}} + \Delta G_{\text{ion}} \quad (1)$$

where ΔG_{mix} is the free energy of mixing of the polymer chains with the solvent medium, ΔG_{elas} is the free energy of elasticity of the cross-linked network, and ΔG_{ion} is the ionic electrostatic energy due to the Donnan equilibrium and electrostatic repulsions between charged side groups on the polymer backbone. Hydrogels that do not contain charged side groups on the polymer backbone do not change volume upon exposure to CrO_4^{2-} in solution, as shown in the control experiment in Figure 2. This is consistent with the observations from Asher's group.²⁸

As for the microcantilever modified with hydrogels that contain ATAC component, the downward bending of the microcantilevers suggests a shrinking of the hydrogel in response to the presence of CrO_4^{2-} in the solution, as shown in Scheme 2. Figure 4 shows two pictures of an ATAC copolymerized hydrogel taken from a 0.001 M of NaCl solution and from a solution of 10^{-5} M Na_2CrO_4 in 0.001 M NaCl, respectively. The hydrogel contracted $\sim 30\%$ in response to the presence of CrO_4^{2-} (based on the change in the longest dimension). Since most hydrogels are relatively homogeneous materials that shrink or swell uniformly, with no dramatic change in shape, the microcantilever bending is reversible and reproducible.

The maximum CrO_4^{2-} concentration in our experiments was at 10^{-4} M, and the ionic strength changed $\sim 30\%$ ²⁹ from a 0.001 M NaCl solution to a solution of 10^{-4} M CrO_4^{2-} in 0.001 M NaCl. In all other CrO_4^{2-} solutions, the ionic strength differences with the 0.001 M NaCl electrolyte solution were $< 3\%$. The effect of such a small change in ionic strength on microcantilever bending can be neglected. Variation in pH can change the hydrogel volume.³⁰ However, in our experiments, the pHs of all the solutions were 7.0, which argues against the pH effects on the hydrogel shrinking as an explanation for our observations. Thus, it appears that the observed ATAC copolymerized hydrogel shrinkage may be due primarily to an osmotic pressure decrease that arises from the ion exchange equilibrium of CrO_4^{2-} for chloride, ion-paired with the quaternary ammonium groups in the hydrogel, as shown in the following reaction.



The ion pair formation between CrO_4^{2-} and the quaternary ammonium groups of a SAM-modified cantilever was postulated to be responsible for cantilever bending.⁵ Prior to the introduction of CrO_4^{2-} into the solution in contact with the cantilever, Cl^- ions are associated with the quaternary ammonium cations. As illustrated in eq 2, the sorption of CrO_4^{2-} in solution requires two quaternary ammonium molecules in the hydrogel to maintain electrical neutrality. A smaller number of counter CrO_4^{2-} anions, one CrO_4^{2-} per two quaternary ammonium sites, are absorbed, causing the decrease of osmotic pressure from a Donnan-type potential and, subsequently, shrinking of the hydrogel. When the

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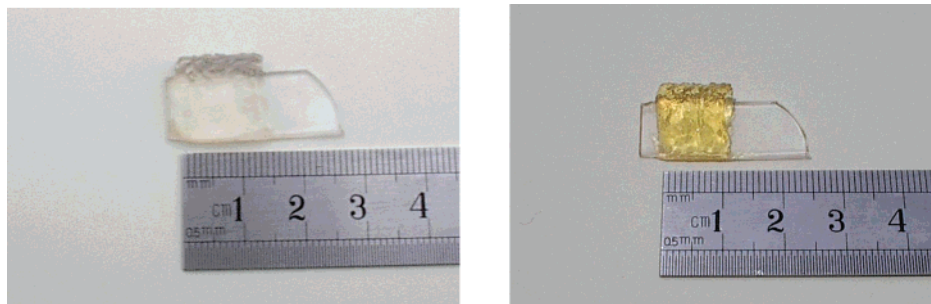


Figure 4. Pictures of an ATAC copolymerized hydrogel equilibrated with a 0.001 M NaCl solution for 2 days (left) and equilibrated with a solution of 10^{-5} M Na_2CrO_4 in 0.001 M NaCl overnight (right). The hydrogel on the right is yellow as a result of the absorption of CrO_4^{2-} . The transparent support is a quartz plate.

solution in contact with the hydrogel was replaced with NaCl, the quaternary ammonium ion pair converted back to $\text{R}_4\text{N}^+\text{Cl}^-$, which expanded the hydrogel.

Since the hydrogel film was relatively thick ($15\ \mu\text{m}$), it took hours for the whole film to reach the equilibrium in different CrO_4^{2-} solutions. To obtain a fast response, for each measurement in our experiments, a 0.5-mL buffer solution was injected into the fluid cell, and it took 7.5 min for the injected solutions to flow through the fluid cell, after which the original buffer solution was circulated back into the fluid cell. In consequence, only part of the ammonium groups in the polymer interacted with the CrO_4^{2-} in the solution, and the maximum response shown in Figures 1 and 2 did not provide a full picture of the microcantilever's actual response at equilibrium at each CrO_4^{2-} concentration.

The selectivity of this cantilever for CrO_4^{2-} over other anions can be explained^{5,31,32} by the hydration energy of CrO_4^{2-} . The hydration energy of CrO_4^{2-} is smaller than that of other anions, such as Br^- , HPO_4^{2-} , NO_3^- , Cl^- , and CO_3^{2-} . These anions with higher hydration energies have a weaker association with the quaternary ammonium cation. After the CrO_4^{2-} solution is introduced, the Cl^- is displaced by stronger ion pair formation between CrO_4^{2-} and the quaternary ammonium cation. This explanation also provides an alternative, but equivalent, explanation for shrinking and swelling of the hydrogel layer that is more phenomenological in origin. Simply stated, the exchange of a highly hydrated anion, such as Cl^- , for a less hydrated anion, such as CrO_4^{2-} , contributes to a decrease in the volume of water within the pores of the hydrogel, leading to a decrease in the volume of the gel.³¹

Significant microcantilever bending that occurs following exposure to the divalent CO_3^{2-} and SO_4^{2-} anions at high

concentrations may be attributed to the smaller size of the CO_3^{2-} and SO_4^{2-} , as compared to CrO_4^{2-} . The radii of CrO_4^{2-} , SO_4^{2-} , and CO_3^{2-} are 2.29, 2.18, and 1.89 Å, respectively.³³ The smaller 1:2 ion pair between CO_3^{2-} or SO_4^{2-} and tetraalkylammonium ions shrinks the hydrogel to a greater extent than CrO_4^{2-} . However, the higher threshold concentration of CO_3^{2-} or SO_4^{2-} reflects the greater selectivity of the quaternary ammonium modified hydrogel for CrO_4^{2-} .

CONCLUSIONS

Our study has shown that a hydrogel-modified cantilever can selectively respond to CrO_4^{2-} at concentrations as low as 10^{-11} M. The sensitivity for detection of CrO_4^{2-} using a hydrogel-modified cantilever is much higher than the ISE method. Hydrogels, containing various molecular recognition receptors, could potentially be a general method for modification of the surface of microcantilevers for the detection of many chemical and biological species, because hydrogels have the property of converting chemical and electrical energy into mechanical energy.

ACKNOWLEDGMENT

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