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# Detection of pH variation using modified microcantilever sensors

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## Abstract

A micromechanical technique for measuring solution pH using modified silicon ($SiO_2$) and silicon nitride ($Si_3N_4$) microcantilevers is described. As the modified surface of the cantilever accumulates charge proportional to the pH of the surrounding liquid, the cantilever undergoes bending due to the differential surface stress. Results are presented for chemically modified (4-aminobutyltriethoxysilane, 11-mercaptoundecanoic acid) and metal-modified (Au/Al) surfaces over a pH range 2–12. Aminosilane-modified $SiO_2$/Au cantilevers performed robustly over pH range 2–8 (49 nm deflection/pH unit), while $Si_3N_4$/Au cantilevers performed well at pH 2–6 and 8–12 (30 nm deflection/pH unit). The influences of other ions on cantilever bending were found to be negligible below $10^{-2}$ M concentration.

*Keywords:* Microcantilevers; pH; Surface stress; Microcantilever bending

## 1. Introduction

Microcantilevers designed for atomic force microscopy have been successfully used as extremely sensitive chemical, physical, and biological sensors [1–3]. The resonance frequency of a microcantilever varies as a function of molecular adsorption. A mass sensitivity in the range of 1 pg has been demonstrated by many different groups. Molecular adsorption also induces cantilever bending when adsorption is confined to one surface of the cantilever. We have observed that this effect can be detected even on so-called "real surfaces" such as the surface of a microcantilever exposed to air or liquid. Many chemical and biological sensors can be designed using the adsorption-induced bending of cantilever structures. Using this concept, the feasibility of chemical detection of a number of vapor phase and liquid phase analytes with extreme high sensitivity has been demonstrated [4–8]. The primary advantages of the microcantilever method are sensitivity based on the ability to detect cantilever motion with sub-nanometer precision and the suitability for fabrication into a multi-element sensor array.

The use of cantilever deflection as a means of signal transduction requires modification of one surface of the cantilever. Many selective coatings have been developed for application in quartz crystal microbalance (QCM) and surface acoustic wave (SAW) devices [9]. For example, mercury adsorption on gold-coated microcantilevers has been detected with ppb sensitivity. Many different chemicals have been detected using chemically selective coatings applied to one surface of the cantilever. Recently, chemically modified microcantilevers have been used to detect chemical species under solution. Earlier, we have reported the detection of cesium ion concentration in solution using $SiO_2$/Au cantilevers modified with calix[4]crown-6 ether [10].

In this paper, we report the micromechanical detection of pH using surface-modified microcantilevers. The technique is based on the ionization of surface species on a microcantilever as a function of solution pH. As one surface of the cantilever accumulates charge proportional to the pH of the surrounding liquid, the cantilever undergoes bending due to the differential surface stress. In addition, cantilever surfaces can be selectively modified to respond within a specific pH range. The influence of other ions on cantilever bending was found to be negligible below $10^{-2}$ M concentration. It should be pointed out that the sensitivity of microcantilevers to different pH has been reported before by Butt [11]. No attempts, however, have been made to develop a sensor based on this concept.

## 2. Experimental

We used commercially available, V-shaped silicon nitride and silicon cantilevers with typical dimensions of 200 μm

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length, 40 μm width, and 0.7 μm thickness in these experiments (available from Digital Instruments, CA, and Park Scientific, CA). The cantilevers were first degreased and stripped of gold. A fresh 20 nm layer of gold was later evaporated on one side of each cantilever. To assure the adhesion of gold onto silicon or silicon nitride cantilevers a thin 3–8 nm chromium layer was vacuum evaporated prior to gold deposition. $Al_2O_3$/Au cantilevers were made by evaporating 20 nm aluminum onto the silicon side of the cantilever (other side gold) and stored at room temperature overnight until all the Al thin film oxidizes to $Al_2O_3$.

The bending of the cantilevers was measured with sub-Angstrom resolution using the optical beam deflection technique. In the optical beam deflection method, the bending of the cantilever is measured by monitoring the position of a laser beam reflected off the upper side of the free cantilever onto a four-quadrant photodiode. The output from the photodiode can be used for measuring the resonance frequency, resonance amplitude, and bending of the cantilever simultaneously. The sensitivity of the detection was determined to be 10.58 mV/nm by pushing a silicon nitride cantilever against a solid surface using a calibrated piezoelectric element. The sensitivity term deviated slightly for different cantilevers depending on the coating. The variation, however, was less than 10%.

The chemicals used such as 4-aminobutyltriethoxysilane, EtOH (99.5%), HCl, NaOH (99.99%), and $CH_2Cl_2$ were used as received from Aldrich, while 11-mercaptoundecanoic acid was synthesized according to procedure described in [20]. High-purity de-ionized water was obtained with a Milli-Q water system (Millipore). For chemical modification, both the $Si_3N_4$ and $SiO_2$ cantilevers (with Au on one side) were cleaned in piranha solution (7:3 $H_2SO_4$ (96%):$H_2O_2$ (30%)) for 30 min and rinsed with $H_2O$ (three times) and EtOH (two times) before measurement or SAM preparation. Aminosilane-coated Au/$SiO_2$ cantilevers were prepared by dipping the cleaned cantilever tip into 1% 4-aminobutyltriethoxysilane in EtOH:$H_2O$ (95:5) solution overnight; cantilevers were rinsed with EtOH three times. The coating of 11-mercaptoundecanoic acid on the gold took two steps. First, cleaned Au/$SiO_2$ cantilevers were immersed into $10^{-3}$ M 11-mercaptoundecanoic acid in $CH_2Cl_2$ for 3 days, then rinsed with $CH_2Cl_2$ three times. Approximately 20 nm of Au was subsequently evaporated onto the silicon side of the cantilever to eliminate the interference of pH interaction on the silicon side.

We have used freshly made pH solutions in our experiment that were prepared by adding varying concentrations of HCl or NaOH to water. The pH of the final solutions was measured using standard pH meter (Beckman Instruments). We have also used pH solutions made from buffer solutions. The experimental results obtained with buffer solutions show that the results are very close to those obtained from HCl or NaOH solution.

## 3. Deflection measurements

The experiments were performed in a flow-through glass fluid cell (Digital Instruments) such as those used in atomic force microscopy. In the glass cells, the cantilevers were held in position using a spring element. Initially, distilled water was circulated through the cell using a syringe pump. It is important to make sure that there are no gas bubbles trapped in the fluid cell. Since the flow rate can change the cantilever bending, a constant flow rate of 10 ml/h was maintained during the entire experiment. Experimental solutions were injected directly into the fluid flow via a low pressure injection port/sample loop arrangement (Upchurch Scientific). This arrangement allowed for continual exposure of the cantilever to the desired solution without disturbing the flow cell or the flow rate. Since the volume of the glass cell including the tubing was only 0.3 ml, a fast replacement of the liquid in contact with the cantilever was achieved.

The deflection measurements were carried out with an AFM photodiode. A schematic diagram of the apparatus used in this study is shown in Fig. 1. The bending of the cantilever is measured by monitoring the position of a laser beam reflected from the cantilever onto a four-quadrant photodiode. The error voltage of the position sensitive detector when the cantilever was immersed in distilled water

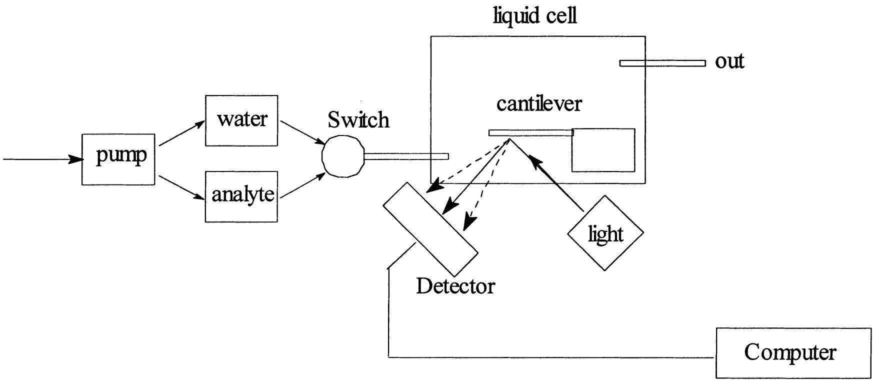


Fig. 1. The schematic of the fluid cell and the cantilever deflection measurement system used in this experiment.

was set as background corresponding to 0 nm. In our experiment, we define 'bending down' as cantilever bending towards the silicon or silicon nitride side while, 'bending up' refers to bending towards the gold side. The precision of an individual cantilever deflection was within 6% as determined by replication measurements.

## 4. Results and discussion

### *4.1. Deflection of Au-coated cantilevers in different pH solutions*

Initially, the cantilever response was recorded for a flow of distilled, de-ionized water. The effect of pH on Au/silicon nitride microcantilever is shown in Fig. 2a where the equilibrium deflection of the microcantilever is plotted as a function of pH. When the pure water was switched to solution with $\mathrm{pH} < 7$, the cantilever bends up towards the Au side. At each pH, the deflection reaches an equilibrium position after ca. 500 s. The cantilever deflection increases as the pH decrease (concentration of $\mathrm{H}^+$ increase). When the solution was switched back to water, the cantilever returns to its original position. When $\mathrm{pH} > 7$, the deflection is towards $\mathrm{Si_3N_4}$ side. The equilibrium deflection of the cantilever as a function of different pH is shown in Fig. 2a. The average deflection of the cantilever is approximately 95 nm/pH.

The cantilever deflection due to variation in solution pH is due to a differential stress caused by the interaction of protons with the surface of silicon nitride. This interaction is a sum of three reactions, which can be described as the following equations [10]:

$$\mathrm{SiNH_2} + \mathrm{H^+} \leftrightarrow \mathrm{SiNH_3}, \quad \text{when } \mathrm{p}K_{\mathrm{a1}} = 10 \tag{1}$$

$$\mathrm{SiO^-} + \mathrm{H^+} \leftrightarrow \mathrm{SiOH}, \quad \text{when } \mathrm{p}K_{\mathrm{a2}} = 8.7^{12}\,\text{or}\,6.2^{13} \tag{2}$$

$$\mathrm{SiOH} + \mathrm{H^+} \leftrightarrow \mathrm{SiOH_2}^+, \quad \text{when } \mathrm{p}K_{\mathrm{a3}} = -1.2^{10}\,\text{or} - 1.8^{11} \tag{3}$$

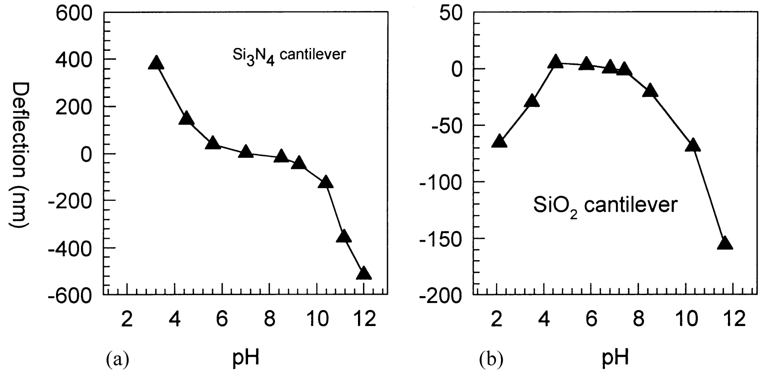
The surface stress responsible for deflection can be caused by all these reactions. In fact, the surface reaction sites would be far more complicated than assumed in this simplified model. These reactions on the surface result in a gradual surface stress increase when pH changes from 2 to 12. A more detailed quantitative calculation on the additional effect of these interactions can be found in the literature [11–15].

The bending response of a silicon (Au/silicon/silicon oxide) cantilever as a function of pH is shown in Fig. 2b. Unlike the pH response of $\mathrm{Au/Si_3N_4}$ cantilever, the deflection versus pH profile indicate that the surface stress of Au/silicon cantilever at $\mathrm{pH} = 4$ is the lowest. The cantilever bends down toward silicon side either when pH increases or decreases from a value of 4.0. On a silicon surface, since there are no $\mathrm{SiNH_2}$ sites, only interactions described by Eqs. (2) and (3) take place [15,16]. The deflection of the cantilever should be due to the sum of all the interactions happening at the surface and the effect of the electrolyte layer on the silicon surface [16].

### *4.2. Deflection of chemically-modified cantilevers in different pH solutions*

Though $\mathrm{Au/Si_3N_4}$ cantilevers demonstrate a relatively good pH sensitivity at high and low pH, its pH sensitivity between 6 and 9 is only 14 nm deflection/pH unit. Since high sensitivity is critical for precise pH measurement, it is necessary to modify the cantilever surfaces with other coatings to enhance the pH response. The modification can be done in such a way that high sensitivity for a specific (wide or narrow) pH range can be achieved. Each experiment was performed on at least five cantilevers. The bending discrepancies due to difference in coverage were avoided by keeping the coating time and surface preparation the same in all the experiments.

Aluminum oxide-coated surfaces have been shown to be sensitive to pH, for example, $\mathrm{Al_2O_3}$ has been used to modify ISFET gate surfaces [17,18]. Its surface $\mathrm{pH_{pzc}}$ is different from silicon and silicon nitride surfaces. A coating of $\mathrm{Al_2O_3}$ on a microcantilever should then dramatically change the influence of pH on deflection. Fig. 3 shows the deflection of aluminum oxide coated ($\mathrm{Al_2O_3/Au}$) cantilever as a function



(a) (b)

Fig. 2. Bending responses of unmodified cantilevers as a function of pH: (a) silicon nitride ($\mathrm{Au/Si_3N_4}$) cantilever; (b) silicon ($\mathrm{Au/SiO_2}$) microcantilever.

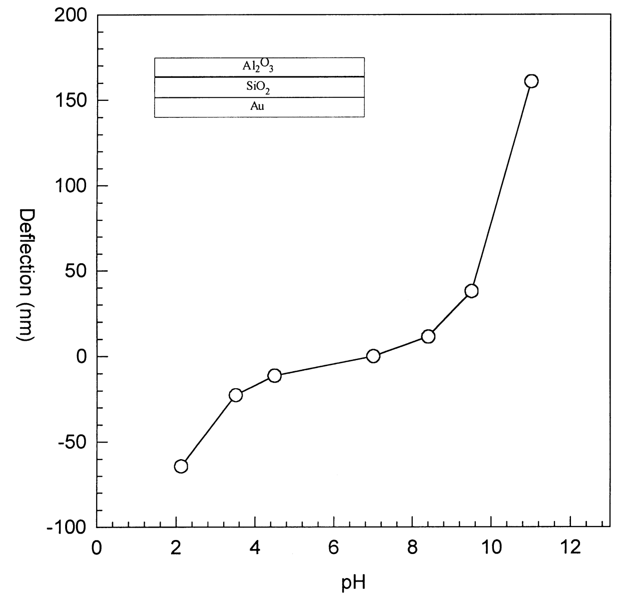


Fig. 3. Bending response of the aluminum oxide coated Au/SiO$_2$ microcantilever as a function of pH.

of pH. The deflection increases with increasing pH, and decreases with decreasing pH over a pH range 4–12. The Al$_2$O$_3$ surfaces are not stable for very long in high or low pH solutions. In low pH solutions, the Al$_2$O$_3$ surface will dissolve into the HCl solution due to reaction with the Cl ion with resultant production of AlCl$_3$, while in high pH solution the surface will dissolve into solution due to chemical reactions that produce NaAlO$_3$, a water soluble product. This would restrict the application of Al$_2$O$_3$/Au/SiO$_2$ microcantilevers to a pH range of between ca. 4 and 12. Rate of deflection is ca. 34 nm/pH unit.

Another approach for sensing pH is to chemically modify cantilever surfaces using a pH-sensitive self-assembled monolayer (SAM). Silane and thiol compounds readily form SAMs on silicon [19] and gold [20] surfaces, respectively, and we can selectively modify one or both surfaces of a cantilever using these compounds. Aminosilane-coated Au/SiO$_2$ cantilevers undergo downward deflection in the pH range 2–9 as shown in Fig. 4. The deflection is nearly linear, with a sensitivity of ca. 49 nm/pH unit. With pH $> 9$, the cantilever also bends downward (towards the silicon side), but the deflection is not significant (<10 nm/pH unit).

The reaction responsible for cantilever stress appears to be the exchange between –CH$_2$CH$_2$NH$_2$ and –CH$_2$CH$_2$NH$_3^+$ activated by solution H$^+$. However, since the SAM may not be confluent, there might be small areas of exposed silicon surface (pin holes) available for interaction with ions in solution. Interestingly, the profile of deflection versus pH shows very similar to the profile of contact angle-pH curve that is also shown in Fig. 4 as comparison with the data from literature [21]. Cantilevers coated with 11-mercaptoundecanoic acid (thiol specific for initial gold side, thiol SAM/Au/SiO$_2$/Au final conformation) performed well in the pH range 2–6 (Fig. 5). The deflection is attributed to the interaction of H$^+$ and OH$^-$ ions in solution with the terminal –COOH group of the thiol compound. The rate of deflection was ca. 16 nm/pH unit.

It is evident that the deflection of silicon and silicon nitride cantilevers in solution is greatly influenced by the presence of metallic and chemical coatings that are restricted to one side of the cantilever, hence creating a differential surface stress on the cantilevers when exposed to solutions of various pH. Of the cantilevers and coatings employed in this study, the best sensitivity and response range were obtained using a combination of Au/Si$_3$N$_4$ and

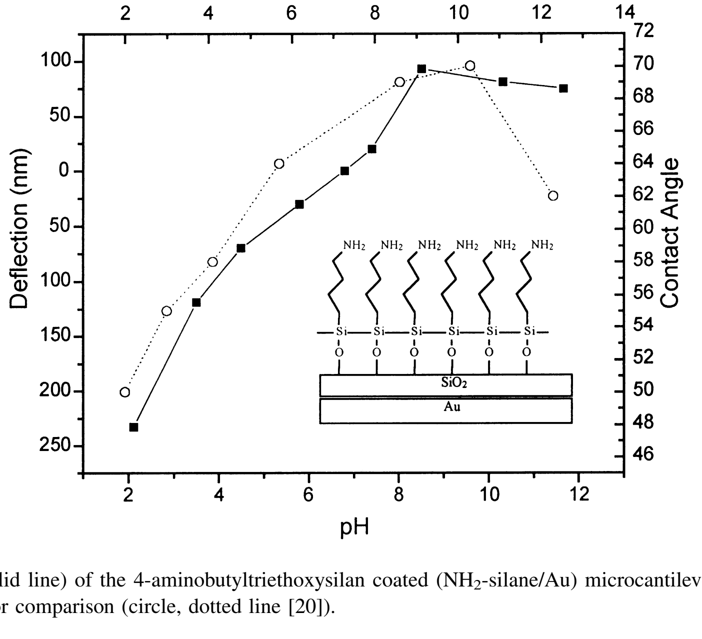


Fig. 4. Bending response (square, solid line) of the 4-aminobutyltriethoxysilan coated (NH$_2$-silane/Au) microcantilever as a function of pH. The contact angle vs. pH profile is also plotted for comparison (circle, dotted line [20]).

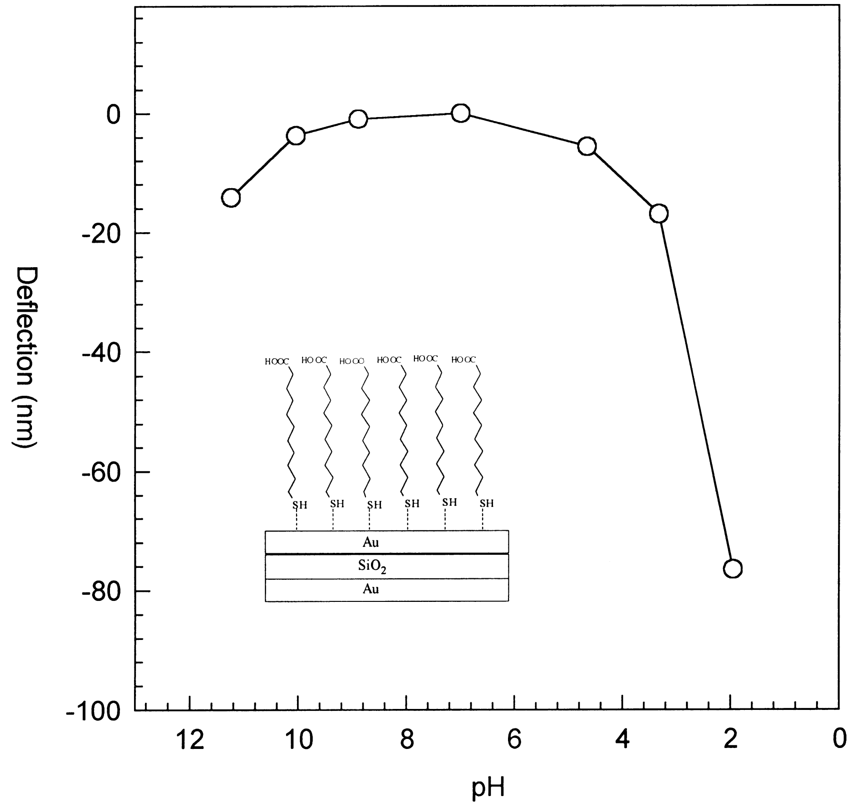


Fig. 5. Bending response of the 11-mercaptoundecanoic acid coated $HOOC(CH_2)_{11}SH/Au$ microcantilever as a function of pH.

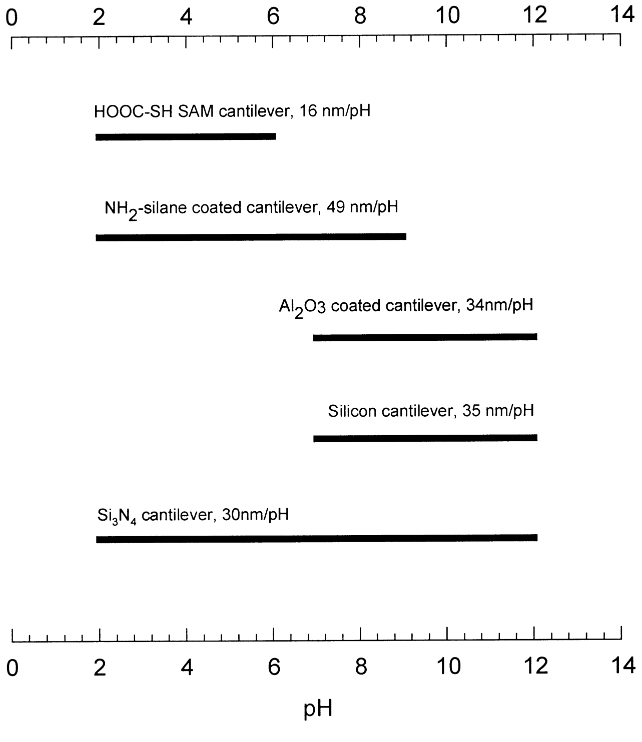


Fig. 6. The pH response region and deflection sensitivity (nm/pH) of different cantilevers used in these experiments.

aminosilane/Au/$SiO_2$ cantilevers (Fig. 6). This combination covered the pH range 2–12 with high sensitivity.

The enhanced sensitivity obtained with triethoxysilane modification cannot be due to multilayer formation. Based on Ito's work, we anticipate that the coating of triethoxysilane modifier is a monolayer [21]. The weaker sensitivity of carboxylic acid SAM coated cantilever may be due to its looser monolayer structure; carboxylic acid head groups at the end of the carbon chain may not pack as rigidly as the other straight chains. Since cantilever deflection is due to surface–surface stress variation, a rigid self-assembled monolayer will produce a stronger cantilever deflection as compared to a loosely packed SAM.

## 5. Conclusions

In this paper, we have demonstrated a novel signal transduction mechanism for pH detection based on modified silicon ($SiO_2$) and silicon nitride ($Si_3N_4$) microcantilevers. Results are presented for chemically-modified (4-aminobutyltriethoxysilane, 11-mercaptoundecanoic acid) and metal-modified (Au/Al) surfaces over a pH range 2–12. Aminosilane-modified $SiO_2$/Au cantilevers performed robustly over pH range 2–8 (49 nm deflection/pH unit), while $Si_3N_4$/Au cantilevers performed well at pH 2–6 and 8–12 (30 nm deflection/pH unit).

It is possible that simultaneous deflection measurements of an array of microcantilevers where each element in the array is modified for certain range of pH can be envisioned. This technique can also be used under solution for detecting biochemical reactions where changes in pH can occur due to formation of certain byproducts. In addition, interesting electrochemical experiments can be conducted in such way that these cantilevers act as working electrodes. Cantilevers coated with metals of different electrochemical potentials can be used to display and investigate electrodeposition, corrosion, as well as solid–liquid interface.

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