

Enhanced chemi-mechanical transduction at nanostructured interfaces

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Abstract

Interfacial molecular recognition processes can be converted into mechanical responses via modulation of surface stress. We demonstrate dramatic enhancement in this transduction when quasi 3-D interfaces with nano-size features are used. Microcantilever surfaces are modified with gold nanospheres or granular films and functionalized with macrocycle cavity and receptors. Deflections of these nanostructured cantilevers in response to vapor phase hydrocarbons are two orders of magnitude larger than with conventional smooth surfaces. Such a significant enhancements of surface stress changes resulting from intermolecular interactions at vapor- and liquid-solid interfaces offer an attractive means to develop novel nano-mechanical devices that respond directly and sensitively to chemical stimuli. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Microfabricated cantilevers that have become commonly used in scanning probe microscopies have become increasingly popular as transducers in chemical and biological sensors [1–7]. This growing fundamental and practical interest in cantilever-based sensors can be explained primarily by two factors. First, a microcantilever transducer directly converts changes in the Gibbs surface free energy created by surface-analyte intermolecular interactions into measurable mechanical responses. Second, the sensitivity of these

cantilevers to small quantities of analytes is superior to that of many other transducers. Using gold-coated cantilevers bearing proper molecular receptors, ultra-low (ppb) concentrations of toxic gases in air [2,4] and metal cations in water [6] have been detected. Other practical applications of cantilever-based sensors can be gained from differential [5] or more sophisticated algorithms [4] applied to responses from cantilevers arranged in arrays. The measurement of changes in surface stress less than 10^{-4} Nm^{-1} is possible when appropriate cantilever designs are combined with sensitive deflection measurements [8,9]. Cantilever deflection is caused by a differential surface stress [10] and, consequently, unequal interaction of the analyte with opposite sides of the cantilever is therefore important. Modification of only one side of silicon or silicon nitride microcantilevers with

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smooth polymer coatings or monolayers of reactive receptors is commonly employed [3–7,11,12]. Our approach, however, consists of creating cantilevers having sides that are both chemically and structurally different. We believe that the creation of nano-sized metal clusters on one side of a cantilever will be especially advantageous in designing chemi-mechanical transducers with large intrinsic enhancements in analyte induced deflection. Colloidal and optical properties of metal clusters organized into two- and three-dimensional (2- and 3-D) structures with submicrometer features have been extensively explored [13–17]. Importantly, similar procedures of receptor immobilization can be applied to smooth and nano-structured gold surfaces [13,15,16]. It is also important to note that cantilever deflection is governed by the same intermolecular and surface forces as those acting in colloids and porous media [18,19] or in small gaps between macroscopic surfaces [18,20,21]. Theoretical evaluations as well as direct measurements of mechanical stresses provide some evidence [18,19] that integral stress in surface-confined colloids may exceed the ‘true’ surface stress of smooth solids by several orders of magnitude.

2. Experimental section

2.1. Chemicals and materials

Triangular, open structure, silicon nitride cantilevers (length 350 μm , thickness 600 nm) were obtained from Park Scientific [11,12]. The silver and chromium metals deposited on the cantilevers were obtained from Alfa Aesar and Kurt J. Lesker Company, respectively, and used as received. The following chemicals were all purchased from Sigma and used as received: the test hydrocarbon analytes, 2,7-dimethylnaphthalene (DMN) and tetrachloroethylene (TCE), and 20 nm gold particles. All other reagents used in these studies were purchased from either Sigma or Fisher Scientific and used as received. All water used to prepare solutions was obtained from a Barnstead E-Pure water filtration system. Ultra high purity nitrogen was used as the carrier gas in all experiments. Heptakis-6-mercapto- β -cyclodextrin (HM- β -CD)

was prepared using the method of Stoddart et al. [22].

2.2. Instrumentation

Cantilever deflection measurements were made by reflecting a 5 mW diode laser (Coherent) operating at 632 nm off the cantilever tip and onto a position sensitive detector (built in-house). The output signal was processed using a lock-in amplifier (Stanford Research Systems). An 1-ml flow cell housing a cantilever holder was used for vapor-phase measurements. TCE and DMN vapors were delivered into the cell via a syringe pump through a T-joint and a 4-way valve, which enabled switching between pure nitrogen and diluted analyte. The degree of analyte dilution was defined by the syringe pump flow rate divided over a total flow rate. The latter was measured at the cell outlet using a mass flow meter tube. The entire instrumental apparatus was located on a vibration isolation table in a thermally controlled environment.

Electrochemical measurements were carried out using a conventional three-electrode cell. The geometrical area of the samples exposed to the electrolyte was in the range of 0.5–2 cm^2 . An Ag/AgCl saturated KCl electrode and a coiled Pt wire were used as reference and auxiliary electrodes, respectively. The data acquisition and voltage control was performed using a CH Instruments 650 A Electrochemical Workstation (CHI version 2.05). Electrolyte solutions for defining the effective surface areas and thiol coverage were 1.0 M H_2SO_4 and 0.5 M KOH, respectively.

2.3. Preparation of cantilever surfaces

Two different technological strategies were used in order to create gold nano-structures on one side of the cantilevers. The first strategy (Process 1 in Fig. 1) involves the deposition of a 40 nm layer of smooth gold followed by electrostatic binding [14] of monodisperse gold nanospheres (with a mean diameter of 20 nm) onto a 4-aminobenzenethiol-modified gold surface. This procedure was performed by coating the cantilevers with the gold layer, 2–3 h immersion in a 1 mg ml^{-1} 4-aminobenzenethiol in methanol solution, and rinsing

with copious amounts of methanol then water. The cantilever was then placed in the solution of gold nanospheres for 1–2 days. The cantilever was then removed from the solution and gently washed with water. The second strategy (Process 2 in Fig. 1) uses chemical dealloying of co-evaporated granular Au:Ag films. This procedure is a thin film adaptation [23] of the method reported by Li and Sieradzki [24] that involves the preferential oxidation of the silver in the alloy. 20–100 nm thick co-evaporated Au:Ag films were used in our studies. The vapor deposition of metals onto the cantilever surface was accomplished using a vapor deposition chamber. The evaporation of a 15 nm gold layer on a 4 nm chromium adhesion layer was followed by co-evaporation of gold and silver until a composite Au:Ag film of the desirable thickness was formed. The deposition rate was 0.04–0.08 nm s⁻¹ and, during co-evaporation, the mass deposition rates were the same for both silver and gold. Both the deposition rates and resulting coating thickness were monitored using a quartz crystal microbalance. The silver was then etched out of the films by placing the cantilever in an aqueous solution of 0.2 w/v % H₂AuCl₄ for 2–3 min.

Chemical modification of the surfaces took place after the surfaces were structurally modified. The surfaces were modified using HM- β -CD in order to form a self-assembled monolayer on the surface. A 1.00 mM solution of the cyclodextrin

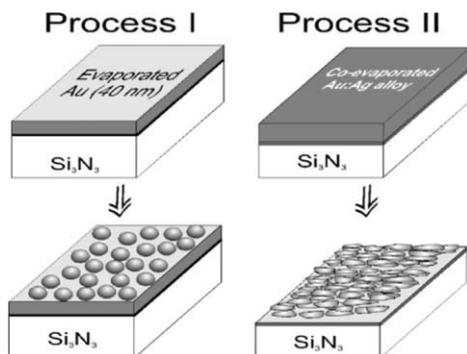


Fig. 1. Schematic illustration of the techniques used in this study to prepare gold nanostructures. Process I and II depict assembly of 20 nm gold nanospheres on a smooth gold surface and formation of the dealloyed gold surface, respectively. The features in the illustration are not drawn to scale.

was prepared in 60/40DMSO/H₂O and deaerated in a vacuum chamber for 30 min. The cantilever surfaces were cleaned using a 40 s immersion in piranha solution (75% H₂SO₄, 25% H₂O₂) to remove any contaminants. The cantilevers were then immersed in the cyclodextrin solution for 18–20 h. Upon removal from the cyclodextrin solution, the cantilevers were rinsed with copious amounts of the DMSO/H₂O solvent.

3. Results and discussion

Fig. 2 shows the atomic force microscopy (AFM) micrographs of the nanostructured surfaces. Although AFM is unable to probe very deep crevices, it clearly confirmed a high density of 20 nm gold spheres (Fig. 2a) assembled on

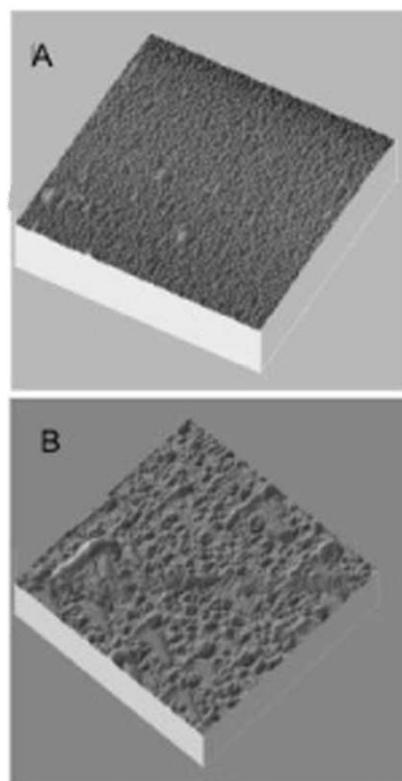


Fig. 2. AFM images of gold nanospheres assembly (panel A) and 20 nm thick dealloyed gold coating (panel B). Both scan areas are 3 × 3 μ m.

aminobenzenethiol-modified gold surfaces and larger irregular gold clusters formed as result of dealloying Au:Ag films (Fig. 2b). To complement the topographic information provided by AFM, scanning electron micrographs of dealloyed surfaces were also obtained [25]. An apparent feature of the nanostructured samples from these micrographs is their increased surface area. More importantly, some of the narrower gaps between gold particles are of the size favorable for involvement of short-range van der Waals, solvation, and steric forces [18]. These quasi 3-D nano-structures may be interpreted as surface confined colloids rather than porous solids. For the dealloyed gold samples, crevices that are narrow and may permit strong short-range repulsive or attractive forces upon adsorption of guest molecules are apparent. The total surface area of such crevices increases with increasing thickness of the dealloyed layer. Both the size and the density of the surface confined gold particles increase in the following order: (i) assembly of 20 nm Au-nanospheres, (ii) 20 nm thick dealloyed gold, (iii) 50 nm thick dealloyed gold (not shown in the figures) and (iv) 75 nm thick dealloyed gold. Based on the AFM data, the roughness (RMS value) of the samples in this series were, respectively, 8, 13, 35 and 45 nm.

Gas-phase measurements were conducted on cantilevers with three types of gold surfaces: smooth, gold nanosphere-modified, and dealloyed. In most cases the gold surfaces were covalently modified with HM- β -CD. Molecular recognition properties of β -cyclodextrin and analogous compounds have been confirmed gravimetrically [26], optically [23] electrochemically [27] and using capillary electrophoresis [28].

Fig. 3 shows the responses of the cantilever to DMN in terms of deflection of the cantilever tip. Deflection is also converted to effective differential stress, $\Delta\sigma^{\text{eff}}$, using the Stoney's Equation (10) as shown in the figure. The response of the cantilever with smooth gold to 83 ppb of DMN (curve a) was approximately the same as that for cantilevers with Au-nanosphere assembly (curve c) or with 20 nm dealloyed gold (curve b) exposed to 10 times less concentrated analyte (i.e. 8.3 ppb DMN). Therefore, a 10-fold increase of adsorbate-induced differential stresses generated on cyclodextrin-

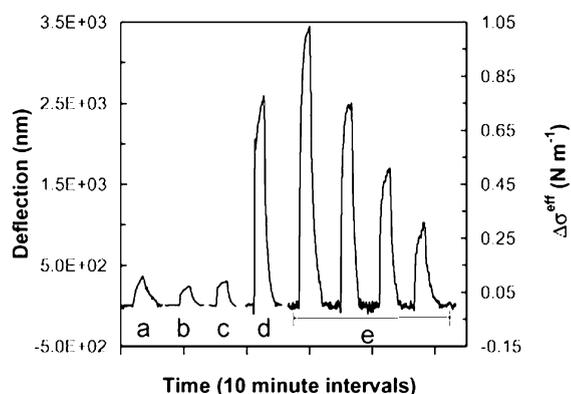


Fig. 3. Enhanced responses of β -cyclodextrin modified cantilevers to DMN as a result of nanostructuring the gold-coated side. The responses are for 83.0 ppb DMN on smooth gold (a), 8.3 ppb DMN on 20 nm dealloyed gold coating (b), 8.3 ppb DMN on 20 nm gold nanosphere assembly (c); 8.3 ppb DMN on 75 nm dealloyed gold coating (d), 8.3, 5.5, 2.8, and 1.4 ppb DMN on 50 nm dealloyed gold coating (e).

modified cantilevers is readily achievable by structuring the gold side of the cantilever. There is even a further deflection enhancement (curves d and e) when the thickness of the nanostructures increased. Fig. 3, curve e also shows a linear decrease in response as the concentration of DMN is decreased. A typical correlation coefficient for calibration plots obtained with the nanostructured surfaces is 0.997. An increased dynamic range due to the increased sensitivity is observed.

Fig. 4 provides a comparison of the response factors (nm of deflection per ppm) for the two test analytes for smooth and nanostructured MCs with immobilized receptor phases. Nanostructuring influences the observed selectivity as the best response for DMN was observed with the 50 nm dealloyed cantilever while the thicker 75 nm dealloyed cantilever provided the largest response to TCE. Note also that a simple monolayer of mercapto-ethane provides responses to these analytes. However, the sensitivity is considerably less than with the equivalent nanostructured cantilever with cyclodextrin receptor. Selectivity as indicated by relative chemi-mechanical responses to the two analytes is also considerably larger for the cavity and receptor (2500 versus 200 for mercapto-ethane cantilever).

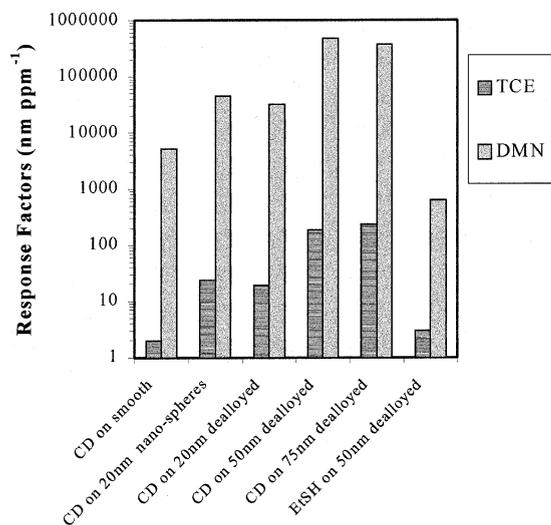


Fig. 4. Comparison of the sensitivities of receptor coated MCs for the two test analytes. In one case the immobilized phase was mercapto-ethane and in the other cases the HM- β -CD.

Enhancement factors (response factor for nanostructured cantilever/response factor for smooth gold cantilever) and limits of detection (LODs, based on a signal three times the baseline noise of 20 nm deflection) were determined from calibration plots for serial dilutions of DMN and TCE. These values appear in Table 1. In the best cases, the enhancement factors were about two orders of magnitude and the LODs are in mid-part-per-billion range for TCE and very impressive mid-part-per-trillion range for DMN.

Independent experiments were performed to verify that the observed increased response with nanostructuring exceeds the increased available

receptor phase on the dealloyed surface. Our surface plasmon resonance experiments revealed that the HM- β -CD bound to smooth gold surfaces with a density slightly exceeding a monolayer. Inspection of the gold(III) oxide reduction wave in cyclic voltammograms of smooth and 50 nm dealloyed gold surfaces indicated a 13-fold increase in surface area with nanostructuring. Using the voltametric method reported by Porter and coworkers for the oxidative desorption of alkylthiols from gold surfaces [29], we obtained surface coverages of 1.7×10^{-9} and 10×10^{-9} mol (thiol group)/(cm² geometric surface area) for the smooth and 50 nm dealloyed surfaces, respectively (note: Porter observed coverages of about 0.9×10^{-9} mol/cm² for alkylthiols). Conversion of these numbers to moles of HM- β -CD per surface would require knowledge of the average number (of the 7 available) thiol groups involved in surface binding. Assuming that this number is the same for both types of surfaces, there is approximately a 6-fold increase in available receptors with nanostructuring of cantilevers. The fact that this number is less than the apparent increase in surface area indicates limited access of the moderately large macrocycle receptor to gold surfaces found in narrow crevices. Similarly, this highlights the contribution of surface stresses associated with short-range steric forces upon DMN and TCE binding to receptors in these confined spaces to the observed large cantilever responses. Additional proof response enhancements clearly exceed the increase in available receptor phase when comparing conventional to nanostructured microcantilevers.

4. Conclusions

We have shown that the asymmetric nanostructuring of cantilever surfaces can lead to two orders of magnitude enhancements in chemi-mechanical transduction. The magnitude of the effective surface stresses generated at the quasi 3-D interfaces significantly exceeds surface free energies of common solids as well as adhesion energies of coating-substrate pairs frequently used in chemical sensors. The demonstrated micrometer-scale movements of the nanostructured cantilevers

Table 1
Comparison of limits of detection, LOD, and enhancement factors, EF, (relative to smooth gold cantilevers) for nanostructured surfaces with HM- β -CD receptor phases

Compound	Surface	LOD	EF
DMN	Gold Beads	1.5 ppb	9
	20 nm dealloyed	2.0 ppb	6
	50 nm dealloyed	0.14 ppb	93
	75 nm dealloyed	0.17 ppb	73
TCE	gold beads	2.8 ppm	12
	20 nm dealloyed	3.4 ppm	10
	50 nm dealloyed	0.34 ppm	97
	75 nm dealloyed	0.28 ppm	120

are especially attractive as a platform for passive chemically controlled microfluidic systems powered exclusively by energy of analyte-device molecular interactions. Because the implemented asymmetric nanostructuring only slightly increases the deflection noise of the cantilever in equilibrium, it also provides an approach to sensors with significantly improved limits of detection and dynamic range. Since different types of nanostructures lead to different enhancement factors with respect to different chemicals, nanostructuring of cantilever surfaces can also create new modes of response selectivity. In comparison to several other coatings investigated in our study, dealloyed gold provided the most efficient transduction of chemical stimuli into mechanical responses. The implemented technology of dealloyed gold is highly compatible with conventional microfabrication and, we believe, can be extended to a great variety of other materials. Therefore, cantilever-based transducers with nanostructured surfaces described herein will have a broad impact on the future development of micro- and nano-fabricated chemical sensors, actuators and integrated 'lab-on-chip' devices.

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