Poster

TOWARDS THE CONTROLLED NANOMECHANICAL ACTUATION OF MICROCANTILEVERS USING REDOX REACTIONS IN ELECTROACTIVE SELF-ASSEMBLED MONOLAYERS

Lana L. Norman and Antonella Badia

FQRNT Center for Self-Assembled Chemical Structures and Department of Chemistry, Université de Montréal, C.P. 6128 succursale Centre-Ville, Montréal, QC H3C 3J7 Canada
Lana.norman@gmail.com

The vertical bending or deflection of surface-functionalized microcantilevers provides an ideal platform for nano- and micro- mechanical actuation and highly sensitive sensing technologies.[1] The basic principle arises from a chemical or physical event occurring on one face of the microcantilever generating a differential surface stress change that is manifested as a bending away from the equilibrium position. The transduction event can be monitored in real-time with considerable sensitivity via an optical beam reflected from the free end of the microcantilever. The deflection is directly proportionally to the surface stress through a modified form of the Stoney's equation and by definition a *compressive stress* (negative surface stress) corresponds to an expansion of the microcantilever, whereas a *tensile stress* (positive surface stress) corresponds to a contraction.[2,3] Over the last decade, a number of nanomechanical systems that employ microcantilevers have been successful in transferring molecular phenomena into macroscopic-scale motion. One of the first and ground breaking examples was the translation of DNA hybridization into nanomechanical motion by Fritz et al.[4] While biomolecular interactions are highly specific and evolve under mild aqueous conditions, their inherent complexity renders the exact origin of the surface stress difficult to ascertain. Key to the development and implementation of microcantilever-based technologies is the ability to control the directional motion with known precision and amplitude. In turn, this requires a comprehensive understanding of the parameters which dictate the origin of the surface stress. To this end, we have investigated the mechanism of the redox-induced deflection of microcantilevers using model self-assembled monolayers (SAMs) of electroactive ferrocene-terminated alkylthiols.

Ferrocenylalkylthiol SAMs are probably the most studied electroactive monolayers and their faradaic electrochemistry is extensively documented in the literature. This is largely because ferrocene SAMs exhibit relatively straightforward electrochemistry meaning that with the appropriate experimental parameters every surface-tethered ferrocene can undergo a one-electron reversible redox reaction. Furthermore, for a compact ferrocene SAM, the dense molecular packing confines the electrogeneration of ferrocenium cations and their complexation with the counterions to the monolayer/solution interface and non-specific ion/solvent permeation across the dielectric monolayer is predominantly inhibited. Electrochemical transformations of surface-confined ferrocenylalkylthiols have previously been shown to elicit dramatic changes in interfacial properties through molecular reorganization or ion complexation controlled/triggered by small external changes in the applied potential.[5,6] In our study, gold coated microcantilevers are functionalized with the redox-active ferrocenylalkylthiols and the origin of the dynamically controlled actuation and surface stress properties are investigated. It is well-known that the selectivity and sensitivity of microcantilever systems rely heavily on the reproducible formation of a functional layer on one surface of the microcantilever,[7] chemically well-defined SAMs provide a relatively simple and versatile system where the amplification of conformational transformations to macroscopically measured deflection can readily be tuned. We clearly demonstrate that the electrochemical transformation of a redox moiety (ferrocene) in the *monomolecular* organic film can generate a surface stress change of a sufficient magnitude to deflect a microcantilever. A characteristic cyclic voltammogram and microcantilever stress profile observed for the redox reaction of the ferrocene-terminated monolayer in a typical electrolyte solution is shown in Figure 1A. Also illustrated in Figure 1B is a schematic representation of the redox reaction that results in the ferrocenium-bearing alkyl chain reorientation giving rise to a lateral force which we propose drives the microcantilever deflection. We will also show that small changes in molecular structure, anion composition and surface concentration of the electroactive redox centers can be used to drive a much larger micromechanical motion in a well-defined and controlled manner, which could have broad implications in micro/nano-electro-mechanical systems.

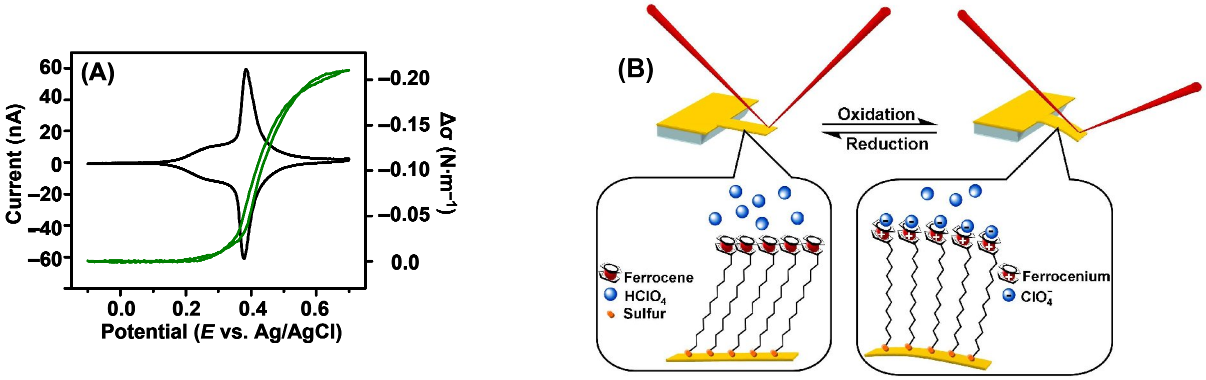

Figure 1. (A) Typical CVs (—) and corresponding differential surface stress, Δ*σ*, (—) response for a $FcC_{11}SAu$ modified microcantilever substrate in perchlorate solution. **(B)** Schematic representation of the proposed mechanism for the $FcC_{11}SAu$ microcantilevers during a redox reaction in perchlorate solution.

[1] Singamaneni, S.; LeMieux, M. C.; Lang, H. P.; Gerber, C.; Lam, Y.; Zauscher, S.; Datskos, P. G.; Lavrik, N. V.; Jiang, H.; Naik, R. R.; Bunning, T. J.; Tsukruk, V. V., Advanced Materials, **20**, (2008), *20*, 653.

[2] Haiss, W., Reports of Progress in Physics, **64** (2001) 591.

[3] Godin, M.; Tabard-Cossa, V.; Grütter, P., Applied Physic Letters, **79** (2001) 551.

[4] Fritz, J.; Baller, M. K.; Lang, H. P.; Rothuizen, H.; Vettiger, P.; Meyer, E.; Güntherodt, H.-J.; Gerber, C.; Gimzewski, J. K., Science, **288** (2000) 316.

[5] Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. Langmuir, **10** (1994) 4380.

[6] Luk, Y.-Y.; Abbott, N. L., Science, **301** (2003) 623.

[7] Tabard-Cossa, V.; Godin, M.; Burgress, I. J.; Monga, T.; Lennox, R. B.; Grütter, P., Analytical Chemistry, **79** (2007) 8136.