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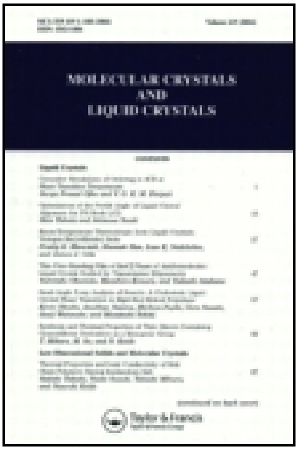

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Monitoring the Electrochemical Transformation of an Azobenzene-Terminated Alkanethiolate Monolayer at Gold by Chemical Force Microscopy

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Chemical Force Microscopy (CFM) was used to study the electrochemical behavior of azobenzene-terminated self-assembled monolayers (SAMs). Both the gold-coated AFM tip and the gold-coated silicon substrate were modified with a 4-((N-(2'-mercapto-ethyl)-amino) carbonyl) azobenzene monolayer. For such a system, only when the reduction/oxidation reaction of azobenzene group occurs, the adhesion force between the tip and sample shows a drastic change, demonstrating the ability of CFM in monitoring the electrochemical transformation of an azobenzene group.

Keywords: chemical force microscopy; self-assembled monolayers

INTRODUCTION

Chemical force microscopy (CFM), which uses a chemically modified AFM tip to induce and/or enhance specific interactions between tip and sample, can serve as a sensitive probe of the variations in chemical interactions and surface energies[1]. A wealth of useful chemical information can be obtained by CFM, including the dissociation and ionization properties[2,3], the spatial distribution[4], and the oxidation state[5] of the surface functional groups.

In this paper, we demonstrate the application of CFM in monitoring the electrochemical transformation of an azobenzene-terminated monolayer.

EXPERIMENTAL

Both gold-coated AFM tips and gold-coated silicon substrates were chemically modified by immersing into an ethanolic solution of 4-((N-(2′-mercapto-ethyl)-amino) carbonyl) azobenzene ($HS\text{-}CH_2CH_2NHC(O)\text{-}\phi\text{-}N{=}N\text{-}\phi$, referred to as AzoC2SH) for 24h[6]. A Nanoscope E scanning probe microscope (Digital Instruments) was used in combination with a Pico-SPM (Molecular Imaging Co.) equipped with a Teflon cell to obtain force curves as the potential applied to the sample was scanned in a cyclic voltammetric experiment. The reference electrode was a silver wire. The tip and substrate were grounded together through a conductive clip, to ensure the simultaneous control of the tip and substrate potential, and to avoid possible long-range Coulombic contributions to the force measurements.

RESULTS AND DISCUSSION

Figure 1(a) and (c) present the cyclic voltammograms of AzoC2SH SAMs on gold with different scan ranges of potential. The scan rate was set to 20 mV/s. During the cyclic voltammetric scan, a series of force curves were recorded at every 2 seconds, which is corresponding to a potential interval of 40 mV. From the force curves, the adhesion force (F_{ad}) was calculated, and was plotted against the applied potential, as shown in Fig. 1(b) and (d). In each figure, the adhesion forces during two scan cycles were plotted. Obviously the change of adhesion force during each potential scan cycle is well reproducible.

Between the potential range from -400 mV to +520 mV vs. AgQRE, the cyclic voltammogram shows the characteristic double-layer charge discharge behavior (Fig. 1a). During the cathodic scan the adhesion force plotted as a function of applied potential shows a slight decrease, and returns to the original value at the end of anodic scan (Fig. 1b), the

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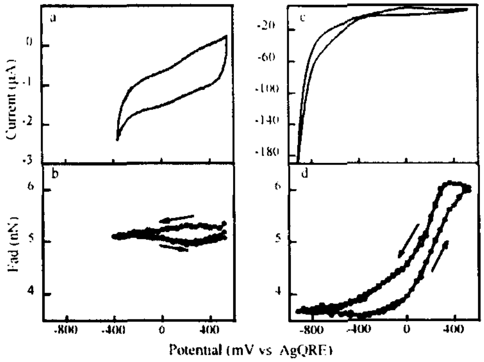

FIGURE 1 (a), (c) Cyclic voltammograms of AzoC2SH SAMs on gold with different potential ranges (scan rate, 20 mV/s; 0.1M $NaClO_4$, pH5.5 phosphate buffer solution). (b), (d) Plots of the force of adhesion vs. applied potential for the cyclic potential scans in (a) and (c), respectively.

maximum change of adhesion force is less than 0.5 nN.

When the potential scan was extended to a range from -920 mV to +520 mV, the cyclic voltammogram shows a pair of redox peaks with a large separation of about 440 mV (Fig. 1c), which corresponds to the reaction of the azobenzene group. During the cathodic scan the adhesion force shows a steep change from 6nN to 3.5nN, and returns to the original value at the end of anodic scan (Fig. 1d). Comparing Fig. 1(d) with Fig. 1(b), we can conclude that the steep change of F_{ad} in Fig. 1(d) is induced by the electrochemical reaction.

However, due to the sharp increase of cathodic current, we are not sure if the steep change of F_{ad} is caused by H_2 formation reaction or by electrochemical transformation of azobenzene group. For this reason, we made a comparative study using an octadecanethiolate monolayer instead of AzoC2SH monolayer. The cyclic voltammogram, in this case, shows only the large cathodic current originating from the H_2 evolution (Fig. 2a). Meanwhile, we do not observe a discernible change in F_{ad} (Fig. 2b). This suggests that the steep change of F_{ad} observed in Fig. 1(d) directly arises from the electrochemical transformation of azobenzene group.

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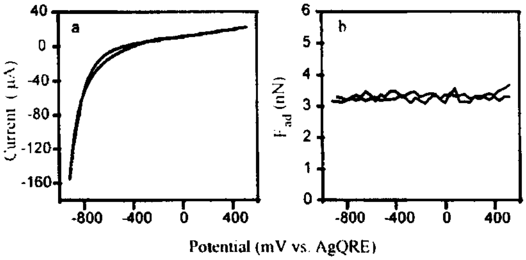

FIGURE 2 (a) Cyclic voltammogram of octadecanethiolate SAMs on gold (scan rate, 20 mV/s; 0.1M $NaClO_4$, pH5.5 phosphate buffer solution). (b) Plot of the force of adhesion vs. applied potential for the cyclic potential scans in (a).

We measure the contact angle for water droplet with the sample being under potential control, which is found to keep almost constant(~71°) upon reduction. This indicates that the remarkable adhesion force change together with the electrochemical transformation of azobenzene groups is not from the solvation energy or miscibility differences between the reduced and oxidized state. A detailed study is in progress.

Acknowledgments

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References

[1] C. D. Firsbie, L. F. Rozsnyai, A. Noy. M. S. Wrighton. and C. M. Lieber, *Science,* **265,** 2071(1994).
[2] D. V. Vezxenov, A. Noy, L. F. Rozsnyai, and C. M. Lieber, *J. Am. Chem. Soc.,* **119,** 2006(1997).
[3] H. X. He, C. Z. Li, J. Q. Song, T. Mu. L. Wang, H. L. Zhang, and Z. F. Liu, *Mol. Cryst. Liq. Cryst.,* **294,** 99(1997).
[4] A. Noy, C. D. Frisbie, L. F. Rosznyai. and C. M. Lieber, *J. Am. Chem. Soc.,* **117,** 7943(1995).
[5] J.-B. D. Green, M. T. McDermott, and M. D. Porter, *J. Phys. Chem.* **100,** 13342(1996).
[6] H. Z. Yu, Y. Q. Wang, J. Z. Cheng, J. W. Zhao, S. M. Cai, H. Inokuchi, A. Fujishima, and Z. F. Liu, *Langmuir,* **12,** 2843(1996).