

LETTERS

Direct Observation of Two Types of Monolayer-Bound Ferricinium Ions on Gold: Implications for Electrocatalysis

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Received: April 18, 2003

The direct surface-enhanced Raman spectroscopic (SERS) observation of two thermodynamically and electrocatalytically different types of ferricinium ions covalently bound to the redox-active monolayer of 9-mercaptononyl-5'-ferrocenylpentanoate (MNFcP) on gold is reported. The presence of different surface redox centers generates an unusual electrocatalytic effect that might be called ion-gated mediated electron transfer. The ion gating is triggered by the substitution of the dominant anion in the supporting electrolyte. In the solution dominated by poorly hydrated ("hydrophobic") perchlorate anions, the mediated electron transfer is sluggish, whereas the highly hydrated ("hydrophilic") fluoride anions sharply accelerate the electrocatalytic electron transfer rate from the substrate (ascorbic acid) to the mediator. SERS data indicate that the inhibition of the mediated electron transfer is strongly related to the presence of the ion pairing between the ferricinium and hydrophobic perchlorate ions. In the fluoride-dominated solutions, at the initial stage of MNFcP monolayer oxidation, the ion pairing is suppressed. Thus, the hydrophilic fluoride ions act as accelerators, but hydrophobic perchlorate ions act as inhibitors of the mediated electron transfer.

Introduction

Ferrocene (Fc)-terminated thiols constitute a large class of metalloorganic compounds capable of forming surface-confined self-assembled monolayers (SAMs). The ability to organize into well-ordered structures, wherein the redox-active terminal can be positioned at a predefined distance from the metal surface, makes this class of SAMs attractive for theoretical electron-transfer studies.^{1–3} Recently, some new utility areas have been suggested for the Fc-SAMs, including the development of molecular electronic devices and electrocatalytic systems.^{4–6} In this communication, we report the direct spectroscopic observation of two thermodynamically and electrocatalytically distinct forms of ferricinium ions (Fc^+) confined to the pure (nonmixed) organic monolayer on the gold electrode surface. The presence

of these two different ferrocene redox centers generates an unusual electrocatalytic effect that might be called ion-gated mediated electron transfer.

Experimental Section

In the experiments, the polycrystalline gold surface was tailored with 9-mercaptononyl-5'-ferrocenylpentanoate [$\text{Fc}(\text{CH}_2)_4\text{COO}(\text{CH}_2)_9\text{SH}$; MNFcP], which, as we showed earlier,⁷ forms a tightly packed redox-active SAM on gold. The working electrodes were gold wires pressed into insulating resin. The electrodes were polished with alumina slurry, sonicated in Millipore water for 10 min, and etched in aqua regia for 2 min. The electrodes for FT-SERS were electrochemically roughened by the scanning potential (0.3 V/s) 50 times between -0.30 and 1.35 V in a 0.1 M KCl aqueous solution. Hereafter, all potentials are relative to the saturated sodium chloride calomel

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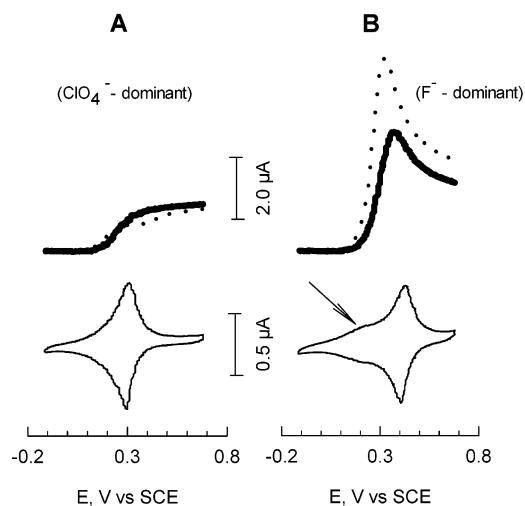


Figure 1. MNFCP-SAM-mediated oxidation of ascorbic acid (AA) on gold. (thin lines) Cyclic voltammograms of MNFCP-SAM. (bold and dotted lines) Background-subtracted voltammograms¹¹ of 1 mM AA oxidation (anodic scans). (Electrolyte solutions) A: 0.1 M NaClO₄ (lines), 1.0 M NaClO₄ (dots); B: 0.5 mM NaClO₄ (lines), 0.1 mM NaClO₄ (dots); both contain 0.1 M NaF. All solutions were buffered with a 0.01 M phosphate buffer adjusted to pH 7.0. Potential scan rate, 0.05 V/s. The gold electrode surface area is 0.04 cm².

electrode (SSCE). The real surface area of the electrodes was estimated from the gold oxide monolayer stripping charge in 1 M H₂SO₄. The SAMs were formed by incubating gold electrodes in a 1 mM MNFCP solution in 95% ethanol for 14–16 h. After the incubation, the electrodes were thoroughly washed with 95% ethanol and Millipore water and were immediately transferred to the working solution. Analytical-grade chemicals were used throughout this work. The electrochemistry part of the work has been carried out on a computerized Versastat (EG&G) electrochemical system. SERS measurements were carried out using a near-infrared FT-Raman spectrometer (Perkin-Elmer, model Spectrum GX) with an excitation wavelength of 1064 nm. The laser beam was focused onto a spot with an area of ~1 mm², and the laser power at the sample was set to 300 mW. To reduce photo- and thermoeffects the spectroelectrochemical cell, together with the working electrode, was swung linearly with respect to the laser beam (~20 mm s⁻¹).⁸ The instrument resolution was 4 cm⁻¹. In this work, none of the presented spectra have been smoothed.

Results and Discussion

Figure 1A (thin curve) shows the cyclic voltammogram (cv) of the MNFCP monolayer recorded in a 0.01 M phosphate buffer (pH 7.0, 25 °C) containing 0.1 M NaClO₄. Even at close to maximal surface saturation ($4.6 \pm 0.4 \times 10^{-10}$ mol/cm²), which is obtained by integrating the cv curve, the MNFCP monolayer exhibits stable redox waves with a formal redox potential (E°_{SAM}) of around 0.30 V.

Water-soluble vitamin C (ascorbic acid, AA; $E^{\circ} = -0.295$ V at pH 7.0) added to the buffer gives rise to a catalytic^{9,10} oxidation wave (Figure 1A, bold curve) in which the half-wave potential $E_{1/2} = 0.26$ V is shifted cathodically with respect to E°_{SAM} . The sigmoid shape of the catalytic wave, according to mediated electron transfer theory,¹¹ is typical for sluggish electron transfer from the substrate (AA) to the mediator (MNFCP-SAM). However, simply replacing the dominant ClO₄⁻ anions in the solution with F⁻ could significantly increase the electrocatalytic efficiency of the MNFCP-SAM. As evident from Figure 1B (bold curve), in the F⁻-dominant buffer,⁹ the

voltammogram of AA oxidation transforms into a peak-shaped curve (half-peak potential $E_{p/2} = 0.28$ V), which is typical for fast charge-transfer processes that are partially or totally controlled by molecular diffusion. Thus, the chemical nature of the anion, which dominates in the supporting buffer, strongly affects mediated electron transfer at the MNFCP-SAM interface as well as redox conversion of the monolayer itself.

Comparing the cyclic voltammograms of MNFCP-SAM reveals several unexpected details. As seen from Figure 1A and B, the decrease in the ClO₄⁻ concentration results in a shift of the main Fc redox peaks toward more positive potentials by about 0.12 V. There is compelling experimental evidence that ion pairing between Fc⁺ and ClO₄⁻ is responsible for this effect.^{12–14} However, in our case, the main peaks, although shifted anodically, result in additional poorly defined current maxima (marked with an arrow in Figure 1B). Such ion-induced “splitting” of the pure Fc-SAM redox conversion has not been previously reported.¹⁵ The new current maximum that is located at around 0.20 V is insensitive to ClO₄⁻ concentration, suggesting that this previously unknown form of surface-bound Fc⁺ differs from the one that readily forms ion pairs with ClO₄⁻.

Another unexpected feature of the electrocatalytic voltammograms is the way in which mediated electron transfer reacts to the variation in ClO₄⁻ concentration. Because the replacement of ClO₄⁻ with F⁻ significantly shifts the main MNFCP-SAM's oxidation peak (Figure 1B), one might expect a similar shift for the catalytic wave of AA oxidation. This is not observed. The position of the catalytic wave remains about the same, but the current sharply increases. The mediated electron transfer in the F⁻-dominant solution is accelerated by a further decrease in the ClO₄⁻ concentration (Figure 1B, dots), whereas the reverse trend is observed in the ClO₄⁻-rich solution (Figure 1A, dots). It appears that the perchlorate-induced shift in the redox potential of the surface-bound Fc switches the mediated electron transfer on and off. We call this phenomenon “an ion-gated mediated electron transfer”.

Thus, the electrochemical data suggests the presence of two different types of surface-bound Fc⁺ groups. It is noteworthy that the existence of kinetically and energetically disperse monolayers has been inferred from the electrochemical experiments.^{2a,3,16} To provide conclusive support for our electrochemical data, we utilized Fourier transform surface-enhanced Raman spectroscopy (FT-SERS) to detect (i) the oxidation state of the surface-bound Fc functionality and (ii) the presence of the ClO₄⁻ ions in an adsorbate layer.¹⁴

Figure 2 shows the difference FT-SERS spectra¹⁷ taken in the F⁻-dominant solution at two potentials: 0.30 V, which corresponds to the poorly defined maximum region of current (marked with an arrow in Figure 1B), and 0.60 V, which corresponds to the almost fully oxidized state of the Fc moiety. In both spectra, two bands at 308 and 1113 cm⁻¹ correspond to the vibrational modes of Fc⁺.^{14,18} Their intensities decrease as the potential becomes less positive, indicating a concomitant decrease of the number of Fc⁺ groups in the monolayer.

The most striking feature of Figure 2 is that, compared to the spectrum at $E = 0.60$ V, the spectrum at $E = 0.30$ V does not contain the vibration band of ClO₄⁻ at 932 cm⁻¹. This experimental fact unambiguously confirms that the SAM is populated with two different types of surface-bound Fc⁺ ions. The band at 932 cm⁻¹ is direct evidence of ion pairing^{6a,7,12b,13,14} between the poorly solvated (“hydrophobic”) ClO₄⁻ anion and Fc⁺. In the perchlorate-dominated solutions, this band is present in FT-SERS spectra at all potentials of the Fc-SAM redox conversion. In the solutions dominated by F⁻, which is known

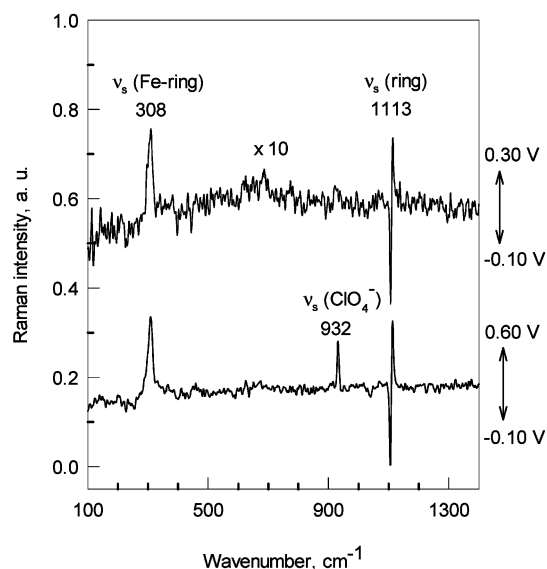


Figure 2. Potential-dependent difference FT-SERS spectra of the MNFcp-SAM on gold in 0.01 M phosphate buffer (pH 7.0) containing 0.5 mM NaClO₄ and 0.1 M NaF. For the upper and bottom difference spectra, 2900 and 200 scans were averaged, respectively. The excitation wavelength is 1064 nm. Laser power at the sample is 300 mW.

to be a highly hydrated (“hydrophilic”) ion, the perchlorate band appears only at high potentials, corresponding to the main redox current maximum. At less-positive potentials, in the poorly defined current maximum region (Figure 1B, arrow-marked peak), the surface is populated with ferricinium ions that do not ion-pair with perchlorate anions. Evidently, these two ferricinium forms mediate electron transfer differently from the substrate (e.g., AA) to the electrode.

What stabilizes the form of Fc⁺ that does not ion-pair with ClO₄[−], and how do we explain the effect of switching the electrocatalytic efficiency on and off by perchlorate? On the basis of our experimental facts, we propose a tentative explanation of this phenomenon. In the early stages of oxidation, when the mean distance between the individual Fc⁺ ions is large and the electrostatic repulsion is weak, the MNFcp-SAM behaves like a flexible 2D structure, and the MNFcp molecules can adopt structural configurations that facilitate fast electron exchange between the substrate, mediator, and electrode. In this initial stage, because of the relatively low fraction of surface coverage, the excess charge of the Fc⁺ ions is compensated by freely diffusing counteranions that dominate the solution (even by highly hydrated, “hydrophilic” anions such as F[−]). In the latter stages, as the surface content of Fc⁺ grows up and lateral electrostatic repulsion increases, only the poorly hydrated ClO₄[−]

ions can penetrate the SAM, forming surface-bound ion pairs or maybe even crystal-like superstructures. The structure of the SAM becomes more rigid, retarding electron exchange between the substrate, mediator, and surface. Thus, in this hypothesis, ion-pairing hydrophobic anions such as ClO₄[−] are molecular inhibitors, and hydrophilic anions are accelerators of mediated electrocatalytic electron transfer.

Acknowledgment. We are thankful to Dr. David Vanderah for fruitful discussions. This work has been partially supported by the Lithuanian State Science and Studies Foundation.

Supporting Information Available: Original background unsubtracted cyclic voltammograms from which the curves shown in Figure 1 were obtained. Cyclic voltammetry curves indicating the good insulating properties of MNFcp monolayers. Cyclic voltammograms of the MNFcp SAMs and electrocatalytic ascorbate oxidation in the buffer solutions without perchlorate ions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Chidsey, C. E. D. *Science* **1991**, 251, 919.
- (2) (a) Tender, L.; Carter, M. T.; Murray, R. W. *Anal. Chem.* **1994**, 66, 3173. (b) Richardson, J. N.; Peck, S. R.; Curtin, L. S.; Tender, L. M.; Terrill, R. H.; Carter, M. T.; Murray, R. E.; Rowe, G. K.; Creager, S. E. *J. Phys. Chem.* **1995**, 99, 766.
- (3) Weber, K.; Creager, S. E. *Anal. Chem.* **1994**, 66, 3164.
- (4) Alleman, K. S.; Weber, K.; Creager, S. E. *J. Phys. Chem.* **1996**, 100, 17050.
- (5) Oh, S.-K.; Baker, L. A.; Crooks, R. M. *Langmuir* **2002**, 18, 6981.
- (6) (a) Uosaki, K. *Electrochemistry* **1999**, 67, 1105. (b) Uosaki, K.; Sato, Y.; Kita, H. *Electrochim. Acta* **1991**, 36, 1799.
- (7) Kazemkaite, M.; Bulovas, A.; Smirnovas, V.; Niaura, G.; Butkus, E.; Razumas, V. *Tetrahedron Lett.* **2001**, 42, 7691.
- (8) Niaura, G.; Gaigalas, A. K.; Vilker, V. L. *J. Raman Spectrosc.* **1997**, 28, 1009.
- (9) See Supporting Information.
- (10) Sabatini, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, 91, 6663.
- (11) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1978**, 93, 163.
- (12) (a) Creager, S. E.; Rowe, G. K. *Anal. Chim. Acta* **1991**, 246, 233. (b) Rowe, G. K.; Creager, S. E. *J. Phys. Chem.* **1994**, 98, 5500.
- (13) Ju, H.; Leech, D. *Phys. Chem. Chem. Phys.* **1999**, 1, 1549.
- (14) Nishiyama, K.; Ueda, A.; Tanoue, S.; Koga, T.; Taniguchi, I. *Chem. Lett.* **2000**, 930.
- (15) The double-peaked voltammograms have been observed in mixed Fc-terminated SAMs and were tentatively interpreted^{12b} as being a result of the partial aggregation of the Fc-SAMs into domains with different local microenvironments.
- (16) (a) Finklea, H. O.; Hanshaw, D. D. *J. Am. Chem. Soc.* **1992**, 114, 3173. (b) Finklea, H. O.; Ravenscroft, M. S.; Snider, D. A. *Langmuir* **1993**, 9, 223.
- (17) The difference spectrum is an algebraic difference between the spectrum recorded at a particular potential, indicated on the right side of the plot, and the spectrum recorded at −0.1 V.
- (18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.