pH-Dependent rectification in self-assembled monolayers based on electrostatic interactions†

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Received (in Cambridge, UK) 20th July 2005, Accepted 14th October 2005
First published as an Advance Article on the web 16th November 2005
DOI: 10.1039/b510270g

Asymmetric electrostatic interactions dependent on pH between the redox molecules and the terminal group on the top of the self-assembled monolayer (SAM) afford control of the electron transfer property of the SAM having the imidazole terminal group.

There has been considerable interest in the development of molecule-based electronic devices as the ultimate challenge in device miniaturization. Because the molecular rectifier is a simple but vital component for molecule-based electronics, various molecules with suitable electronic asymmetry[1,2] have been exploited by several techniques.[3–5] Examples include electrochemical rectification on a chemically modified electrode using redox-active polymers[6] and redox-active monolayers;[7] the common origin of the rectification is the asymmetry in energy level by the immobilized mediator which allows the forward reaction and prohibits the reverse redox reaction. On the other hand, the electrostatic interactions between the charged groups at the surface and electroactive molecules in solution affect the electron-transfer kinetics leading to the current switch,[8–12] and the origin of the reported switches is the symmetry in the electrostatic interaction, where the charged surfaces repel or attract both the reactant/product simultaneously due to the same polarity of the reduced/oxidized form of the redox couple. However, we envisioned that we could construct a molecular rectifier based on asymmetry in electrostatic interactions, exemplified by inward-rectifier potassium channels in cardiac cells.[13]

In this paper we report pH-dependent rectification in SAMs based on electrostatic repulsion. Specifically, imidazole group acts as surface-charge and affect the electron transfer kinetics of the ferrocenemethanol FcOH/$FcOH^+$ redox couple asymmetrically. Scheme 1 depicts the SAM of 1-(12-mercaptododecyl)imidazole† on gold and the control of the direction of electron transfer dependent on pH. When the basic imidazole group on the top of the SAM is deprotonated at high pH, access of both FcOH and $FcOH^+$ to the electrode is allowed, resulting in bidirectional electron transfer (Scheme 1a). At low pH, however, the protonated imidazole group repulses the positively charged $FcOH^+$ and does not exert any force on the neutral FcOH. These asymmetric electrostatic interactions influence the electron-transfer kinetics of oxidation and reduction asymmetrically leading to the rectifying function (Scheme 1b). The reversible protonation/deprotonation of the imidazole group enables the selection between unidirectional and bidirectional electron transfer by adjusting pH.

Cyclic voltammetry was used to determine whether the SAM enables electrochemical rectification. When a potential scan was applied to the modified electrode in an acidic solution, the electron transfer through the monolayer to FcOH was hindered during the first scan. The oxidation current, however, was found to increase during repeated potential scans and a steady CV was obtained after 5–7 cycles of the potential scan,† showing the characteristic feature of electrochemical rectification (i in Fig. 1a). The blocking of the electron transfer in the first scan shows that the order and quality of the SAM is high enough to effectively block electron transfer through electron tunneling, the permeation, and the diffusion.[14] Variation in CV during the following scans suggests the change in the surface structure. The positively charged, bulky imidazole group may induce the reorientation of the SAM during the potential scans as described in previous reports on the dependence of the structure of the SAM on the terminal group and the electrode potential.[15] The steady CV obtained in the following potential scans indicates that the SAM no longer experiences the structural change after 5–7 potential cycles and that the SAM becomes accessible to FcOH while the lack of access of $FcOH^+$ to the electrode is retained. Although the exact determination of the surface structure is impossible at this stage, we believe that further studies would provide more detailed information about the effect of the terminal imidazole groups on the structure of the SAM. After the steady CV was obtained, the pH of the solution was altered repeatedly between 2 and 12 on the same electrode. The typical characteristic CV of an electrochemical rectifier, *i.e.* normal oxidation current and suppressed reduction current, was observed at pH 2 (i in Fig. 1a), while a usual CV of bidirectional electron transfer was obtained at pH 12 (ii in Fig. 1a). There are three important features of Fig. 1a. First, no voltammetric feature corresponding to the reduction of $FcOH^+$ was observed at pH 2, suggesting that the protonated imidazole effectively prevents the access of the positively charged $FcOH^+$. On the other hand, the peak current of the oxidation is as high as that on the naked Au electrode demonstrating the facile access of FcOH. The deviation of the peak current in the anodic and cathodic processes is indicative of the asymmetric electrostatic interactions. Secondly, the peak potential in anodic current is near the oxidation potential of FcOH on the naked gold electrode. In previously reported

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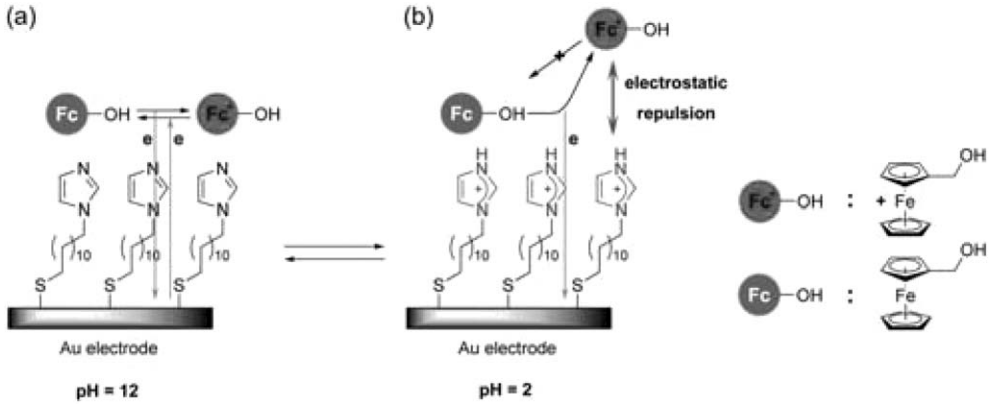
† Electronic supplementary information (ESI) available: synthesis of 1-(12-mercaptododecyl)imidazole, preparation and characterization of the SAM, CV of the SAM-modified electrode during repeated potential sweeps for activation, CVs with the various scan rate, CV of the amine-terminated SAM modified electrode. See DOI: 10.1039/b510270g



Scheme 1 A schematic illustration of pH-dependent rectification. At high pH, the deprotonated imidazole group allows the access of both the oxidized and reduced forms of FcOH as shown on the left side (a). The right side (b) depicts unidirectional electron transfer at low pH caused by the electrostatic repulsion between $FcOH^+$ and the protonated imidazole.

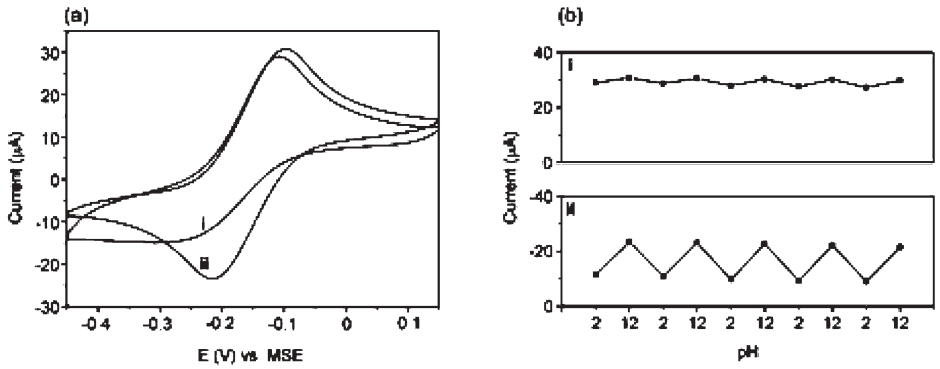


Fig. 1 (a) CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr (i) at pH = 2 and (ii) at pH = 12. Facile oxidation of FcOH and suppressed reduction of $FcOH^+$ is observed at pH 2. The CV at pH 12 has the characteristic features of bidirectional electron transfer. Scan rate = 50 mV s^{-1}. (b) Variation of (i) the anodic peak current and (ii) the cathodic peak current during the repeated alternation of pH.

electrochemical rectifications using mediated electron transfer, the peak potential has been determined by the redox potential of the mediating molecule. In contrast, the peak potential of the electrochemical rectifier based on the asymmetric electrostatic interaction depends on the redox potential of the solution-phase electroactive probe molecule. This feature potentially enables us to set up the onset potential of the rectifying device easily by just exchange of electroactive molecules. Thirdly, reversible switching between unidirectional and bidirectional electron transfer is possible (Fig. 1b). This switching shows that the structure of the SAM induced by potential sweeps is stable during further potential scans and the alternation of the pH. These results demonstrate that the pH-dependent electrochemical rectification based on asymmetric electrostatic interactions has been achieved in our system.

Two different components from the previous electrochemical switches are the key of our system. One is the charge state of the solution-phase redox molecule of $FcOH/FcOH^+$ for the asymmetric electrostatic interactions. The other is the bulky basic imidazole group. When the activation step is performed at pH 12 and when the imidazole group was replaced with a primary amine, the simple blocking effect of the SAM was observed.† These results demonstrate that both the charge interactions and the effects of the terminal groups on the structure of the SAM lead to electrochemical rectification. In addition to the requirements on the electrostatic interaction, the choice of an appropriate terminal functional group on the SAM (*i.e.* the imidazole group) and a suitable redox couple (*e.g.* FcOH) which interacts with the charged terminal is probably crucial to achieving unidirectional electron transfer. Except for the asymmetric electrostatic interaction, another possible mechanism is the conformational change of the SAM induced by the electrode potential.[16] If the positively charged imidazole penetrates into the SAM at the cathodic potential to block the electrode and is detached from the surface at the anodic potential to open the electrode, Fig. 1 can be well explained. Nonetheless, the mechanism of conformational change is improbable at this stage because the spectroscopic data† exhibit the relatively dense SAM hindering such a conformational change. Although there have been many previous examples of electrochemical rectification,[6,7] our unprecedented pH-dependent system is noteworthy because its mechanism of rectification is different from that of mediated electron transfer. Rectification by asymmetric electrostatic interaction does not require complex electroactive functional groups on the surface and provides a simple and versatile strategy for molecular rectification and for other applications such as the ion-channel sensing of chemicals and biomolecules.

To confirm the electrostatic interaction mechanism, CVs were obtained for solutions containing increased concentrations of the

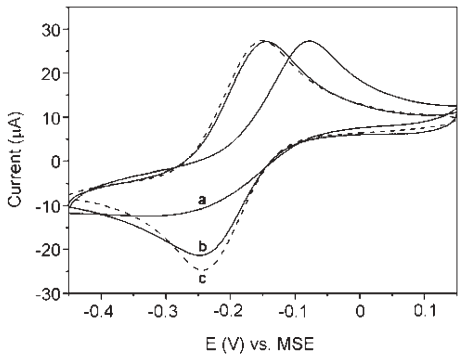


Fig. 2 CVs of the SAM-modified Au in a solution containing (a) 0.5 mM ferrocenemethanol and 10 mM KBr and (b) in 0.5 mM ferrocenemethanol and 50 mM KBr. (c) CV of the naked Au in 0.5 mM ferrocenemethanol and 10 mM KBr. These experiments were performed at pH = 2 with scan rate = 50 mV s^{-1}.

salts. At high salt concentrations, the screening length is too short for each charged molecule to sense the presence of the other molecules. In other words, the supporting electrolyte screens the interactions between the charged molecules. Fig. 2 shows the CVs for higher salt concentrations. Unidirectional electron transfer disappeared due to the screening of the electrostatic interactions caused by the addition of the salts, 50 mM KBr, to supporting electrolyte. These results verify that the rectification is caused by the electrostatic interactions between the ions, which are favored in low ionic strength solutions.[13]

In conclusion, pH-dependent electrochemical rectification based on asymmetric electrostatic interactions was observed on the SAM modified Au electrode. Unidirectional electron transfer is observed at low pH due to the repulsive interaction between the protonated imidazole group and the positively charged $FcOH^+$. In contrast, the neutral, deprotonated imidazole group permits the access of both the neutral FcOH and the positively charged $FcOH^+$, leading to bidirectional electron transfer at high pH. The achievement of this unprecedented and simple pH-dependent rectification based on electrostatic interactions can be attributed to the use of the terminal imidazole group and the neutral FcOH, which has a positive charge after oxidation. This work may provide insights into the design of functional groups on surfaces for molecular electronics and of model systems for molecular recognition and biological channels.

This work was supported by the Korean Ministry of Science and Technology through the Bioelectronics Program (2005-01070) (J.K.), Grant No. R01-2005-000-10503-0 from the Basic Research Program of the Korea Science & Engineering Foundation (J.K.), the National Research Laboratory Program (S.-g.L.), Department of the Airforce in United State (S.-g.L.), the National R&D Project for the Nano Science and Technology (I.S.C. and J.K.) and the Center for Molecular Design and Synthesis (S.-g.L. and I.S.C.). We thank Dr Won at the Korea Basic Science Institute (KBSI) for the XPS analysis.

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