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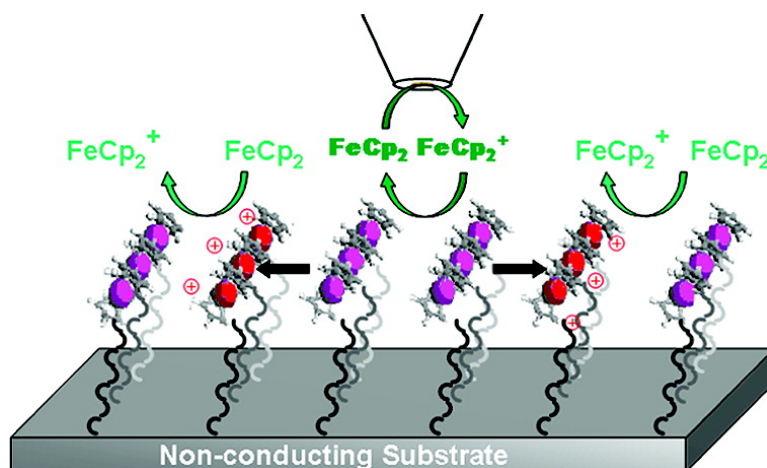
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Conducting Ferrocene Monolayers on Nonconducting Surfaces

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The attachment of functional self-assembled monolayers (SAM) onto insulating, semiconducting, metallic or carbon-based substrates constitutes an attractive approach for building novel interfaces for applications ranging from molecular electronics, photovoltaic devices, and catalysis to chemical/biological sensing.[1-3] A central question concerns the control of mass-transport and charge-transfer processes occurring at monolayer-modified interfaces. In fact, this field raises several more general fundamental questions related to the charge transfer through single molecules or macromolecules and illustrated by the debate about the occurrence of super exchange versus electron hopping.[4] In this connection, common and numerous investigations are based on transient electrochemical methods, such as the simple examination of the response of a reversible redox couple by cyclic voltammetry at the modified surface used as an electrode.[5] When the redox centers are immobilized on the surface, similar procedures could be used and are especially powerful when combined with the use of ultramicroelectrodes.[6] However, these studies provide a global view of the modified surface and are by principle, limited to the investigations made on conducting (or semiconducting) substrates. In these experimental conditions, the control of the electron transfer (ET) may have several origins and may involve different pathways, typically: tunneling through space or through the organic layer to the substrate, direct electron transfer between the surface and the redox molecules in solution, charge exchange between redox active species immobilized at the surface. Because of the conducting nature of the substrate, the estimation of each contribution is generally difficult and often simply reflects the transport of the redox probe through pinholes or defects in the grafted layer.[7]

Since the pioneering works of Bard and Mirkin, scanning electrochemical microscopy (SECM) has been demonstrated to be a powerful tool for analyzing such surface modifications.[8] The major difference with the other classical electrochemical methods is that the surface is locally probed from the solution side with a dissolved redox mediator and thus permits the characterization of layers deposited on a large variety of surfaces. Concerning our study, by using a surface in insulating conditions, one could expect to eliminate the contribution of the substrate in the transport mechanism. This could provide a way for evaluating the different ET pathways' contributions, as well as the measurements of ET kinetics between attached and dissolved redox species. In other words, SECM can be used to probe electroactive species grafted onto an insulating substrate. However, with such surfaces, the difficulty is that the control of the quality of the redox layer during its preparation, as commonly done by classical electrochemistry, is not possible anymore. To circumvent this problem, we chose n-type Si(111) substrates covalently modified with an oxidizable ferrocene center-terminated alkyl monolayer. For oxidation processes, n-type silicon behaves as an insulator in dark and as a quasi-conductor upon illumination, providing a way to switch the contribution of the surface in the ET. The covalent derivatization of Si(111) by a ferrocene-functionalized monolayer has been previously described and is detailed in the Supporting Information (scheme S1).[9] The procedure yields a densely packed monolayer with a surface coverage of ca. 3.5×10^{-10} mol of ferrocene cm^{-2}, i.e. ca. 0.25 bound ferrocene per surface silicon atom.[9]

The voltammetric analysis of the modified surface in dark conditions (Figure 1) shows the absence of faradaic current response. Further addition of ferrocene in the solution did not modify the signal as expected for a nonconducting electrode. Upon illumination, a well-defined reversible wave of the ferrocene/ferrocenium couple appears at $E^{\circ\prime} = 0.25 \pm 0.01$ V vs SCE. As predicted for surface-confined redox species, the peak-to-peak separation ΔE_p is close to zero (20 mV), and the ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}) is close to unity.[5] This result demonstrates the presence of an ideal electroactive layer and that electron transfer from the ferrocene headgroups to the surface is fast and efficient when the substrate is able to accept positive charges.

To get information about the sole contribution of ferrocene headgroups, SECM experiments were achieved on the same sample using two redox couples, namely the ferrocene/ferrocenium (FeCp$_2$) couple that displays a more positive standard potential ($E^{\circ\prime}$(FeCp$_2$) $= 0.45$ V/SCE) than the grafted ferrocene, and the decamethylferrocene/decamethylferrocenium couple (D-FeCp$_2$) with a standard potential ($E^{\circ\prime}$(D-FeCp$_2$) $= 0.10$ V/SCE) is unable to oxidize the attached ferrocene headgroups. The E°'s of the two mediators are both more positive than the flat-band potential of modified silicon surfaces, and thus, the regeneration of their reduced form at the molecule/n-Si(111) interface is expected not to occur in the dark.[10,11] To check that point, we examined first the n-type Si(111) covalently modified by an organic monolayer in which the ferrocene moieties have been replaced by inactive ethyl groups. As shown in Figure 2A, the normalized current, I_t, at a Pt ultramicroelectrode (UME) tip approaching the ethyl undecanoate monolayer, rapidly diminishes for both mediators, when the distance between the UME and the substrate decreases. This reflects the absence of regeneration of the mediator at the interface (negative feedback).[8] Moreover, both experimental approach curves display a good agreement with the theoretical variation expected for an insulating substrate, demonstrating the insulating properties of the surface under these conditions.

On the contrary, for the n-type Si(111) surface terminated by the ferrocene centers, two different responses are observed, depending on the nature of the mediator (Figure 2B). In the case of decamethylferrocene (D-FeCp$_2$), a negative feedback is also obtained. As for the previous nonelectroactive layer, the experimental curve matches the theoretical behavior expected for the insulating substrate. Contrariwise, when the mediator was ferrocene, FeCp$_2$, the approach curve shows a clear positive feedback and thus the occurrence of continuous electron transfer between the electrogenerated ferrocenium species produced at the UME and the
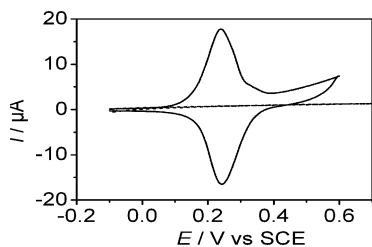
Figure 1. Cyclic voltammograms at 0.1 V s^{-1} of the ferrocene-terminated monolayer in CH_3CN + 0.1 M Bu_4NClO_4 (dashed line) in dark and (solid line) under illumination.
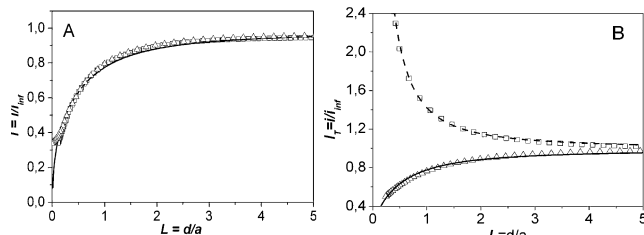
Figure 2. SECM approach curves in dark obtained at a Pt disk UME tip (radius $a = 5$ μm) on two diversely modified n-Si(111) surfaces: (A) n-Si-(111)-$C_{10}H_{20}$C(=O)O-C_2H_5, (B) n-Si(111)-$C_{10}H_{20}$C(=O)NH-C_2H_4-OC_2H_4-FeCp$_2$ using FeCp$_2$ ($\square$) and D-FeCp$_2$ ($\triangle$) at 10^{-3} mol L^{-1} in DMF + 0.1 mol L^{-1} Bu_4NClO_4. The solid and dashed lines are the theoretical curves for totally insulating and conducting substrates cases, respectively.

Scheme 1. Processes Involved in the SECM Measurements of Electron Transfer between an Electroactive Monolayer Bound to an Insulating Surface and a Mediator in Solution: (A) Decamethylferrocene and (B) Ferrocene
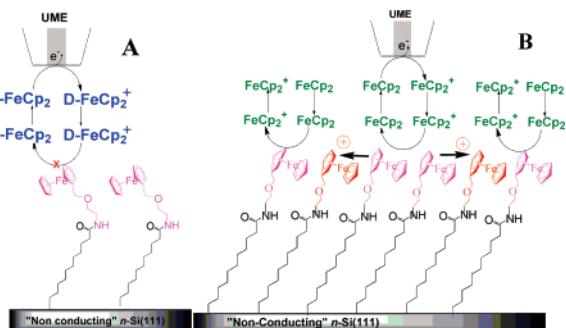
interface. In addition, this curve fits the theoretical curve for a conducting substrate (diffusion control), indicating that the regeneration of the mediator occurs at a very high rate.[8] The observed differences when changing the mediator show the occurrence of an oxidation of the attached ferrocene headgroups by the oxidized mediator FeCp$_2^+$ produced at the UME. Because its $E^{\circ\prime}$ is more positive by 0.20 V than the potential of attached ferrocenes, a fast oxidation of the ferrocene headgroups by FeCp$_2^+$ is now possible. Moreover, considering the insulating properties of n-type silicon in the dark, these results demonstrate that the regeneration of the mediator involves only the attached ferrocene units.

In steady-state conditions on an unbiased sample, in parallel with the continuous oxidation of attached ferrocene by FeCp$_2^+$, the reverse reaction must occur outside the zone where the positive charges are injected to balance the injected positive charges (Scheme 1). This reverse reaction becomes thermodynamically possible

because the potential of the surface is rendered more positive. It follows that the transport of the charges out the diffusion cone of the ultramicroelectrode tip must be a fast and efficient process. In our case, the only possible charge carriers are the attached ferrocene groups. By comparison with similar SECM experiments performed on hydrogenated p-type Si(111), where the charge transport by the silicon substrate is possible,[12] the global process observed here with the ferrocene headgroups, is even faster. We may propose that the charge transport involves a "charge hopping"-type mechanism occurring between adjacent ferrocene groups, as described for redox polymers[7] and more recently for redox dendrimers.[13] In this connection, it is noticeable that fast charging processes were recently reported in giant ferrocenyl dendrimers during their oxidation,[14] suggesting a similar efficient electrochemical communication between the ferrocene groups immobilized on the dendrimer outside edge.

Under our conditions, the 2D-transfer by the ferrocene head-groups is so fast that the determination of electron-transfer kinetics is below the possibilities of our SECM setup. Using a smaller UME, one may expect to determine the kinetics of bimolecular mediated electron transfer between the monolayer-bound and dissolved redox species and the electron communication inside the layer. An exciting result is that this type of monolayer behaves like a purely conducting material. By analogy with the known behavior of giant redox dendrimers,[14] it should be possible to tune the transport properties of the organic monolayer by changing its chemical environment and/or specific interactions between the organic chains (e.g., the surface coverage of redox centers), and consequently the overall electrochemical response. In addition to the interest in fundamental research, this could lead to an interesting concept in designing novel electrochemical sensors and electrochemically switchable devices.

Supporting Information Available: Experimental details for the preparation of the modified Si(111) surfaces and for SECM measurements; CV of the ferrocene n-Si layer. This material is available free of charge via the Internet at http://pubs.acs.org.

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