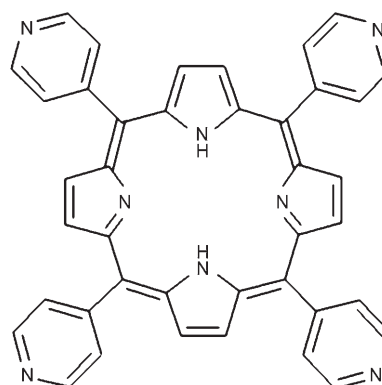# Communications

Dynamics of Porphyrin Electron-Transfer Reactions at the Electrode–Electrolyte Interface at the Molecular Level**

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Electron transfer is an essential step in many important processes and has been the subject of intensive research, with relevance to areas such as molecular electronics, electrochemistry, biology, catalysis, information storage, and solar-energy conversion.[1–4] Therefore, understanding interfacial electron transfer between molecules and electrodes, and their dynamics at the molecular level, is important for fundamental science as well as for technological applications.[5–8] However, the present theoretical and experimental treatment of interfacial electron transfer between molecules and electrodes mainly relies on ensemble-averaged optical spectroscopic and electrochemical measurements.[9] Thus, our understanding of the interfacial electron transfer dynamics at the molecular level is very limited. For example, we do not know how local defects or adsorption sites on a heterogeneous electrode surface affect the dynamics of redox reactions at the molecular level. Nevertheless, it is frequently assumed that reactions principally occur at steps or defects ("active sites"). On a homogeneous surface, is the redox reaction of adsorbed molecules homogeneous? How does the electrode potential affect the spatial distribution of an interfacial redox reaction at the molecular level? How is charge transferred laterally between molecules? Answers to these questions are critical for progress in our understanding. Therefore, there is a tremendous need to probe the dynamics of interfacial electron transfer at the molecular level.

In the experiments reported here, a potential-pulse perturbation was employed to control the electrochemical oxidation of a simple porphyrin (5,10,15,20-tetra(4-pyridyl)-$21H,23H$-porphine (TPyP); Scheme 1) at the Au(111)/0.1 M H$_2$SO$_4$ interface, and scanning tunneling microscopy was employed to provide an insight into the electrochemical oxidation dynamics at the molecular level. TPyP on Au(111) was chosen as a model system for the following reasons:

1) The TPyP molecules can form an ordered monolayer at the Au(111)/0.1 M H$_2$SO$_4$ interface, depending on the electrode potential.[10]

2) The redox states of adsorbed porphyrins on an electrode surface can be distinguished by their different contrast in STM images.[11,12]

3) The adsorption of TPyP onto the Au(111) electrode has a dramatic effect its electrochemical activity. For example,

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Scheme 1. Chemical structure of TPyP.

the reduction of pre-adsorbed oxidized TPyP can be very slow, taking as long as tens of minutes at -0.05 V. However, the oxidation of adsorbed TPyP at 0.2 V is much faster, occurring in seconds. (The potential for the onset of oxidation of adsorbed TPyP is about 0.1 V.)[13]

In the experiment (Figure 1),[14,15] the sample, an adsorbed monolayer of TPyP on Au(111) without TPyP molecules in the 0.1 M H$_2$SO$_4$ solution, was initially held at a potential ($E_1 = $
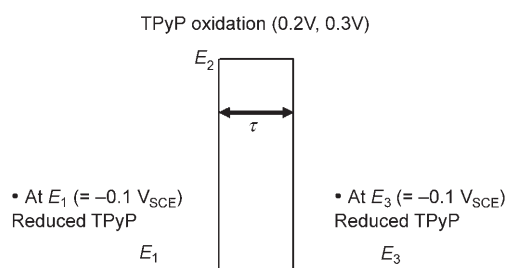

Figure 1. Experimental method: potential-pulse perturbation. SCE = saturated calomel electrode.

-0.1 V) where all the TPyP molecules were reduced.[13] A short oxidation potential pulse (E_2, for duration τ) was applied to the sample during STM imaging. This potential pulse oxidizes some of the pre-adsorbed TPyP molecules. The quantity of oxidized TPyP molecules is determined by the oxidation potential and duration of the oxidation pulse. The duration of the 0.2 V and 0.3 V oxidation pulses employed here ranged from 0.1 s to 1 s. After the oxidation potential pulse, the electrode potential was stepped to $E_3 = -0.1$ V, effectively stopping the oxidation. Reduction of the oxidized TPyP may occur during the process of collecting STM images after the oxidation pulse; however, the rate of reduction of

adsorbed oxidized TPyP molecules at this potential (−0.1 V) is very slow, so that reduction of oxidized TPyP molecules on the electrode surface can be neglected on the time scale of collecting one STM image.[13] Accordingly, we can probe the oxidation rate of TPyP at an Au(111) surface by comparing the number of oxidized TPyP molecules before and after the oxidation potential pulse.

STM can distinguish between the redox states of adsorbed porphyrin molecules on Au(111).[11,12] The STM images obtained at −0.1 V after oxidation potential pulses of 0.2 V of different duration (Figure 2) shows an ordered pattern of
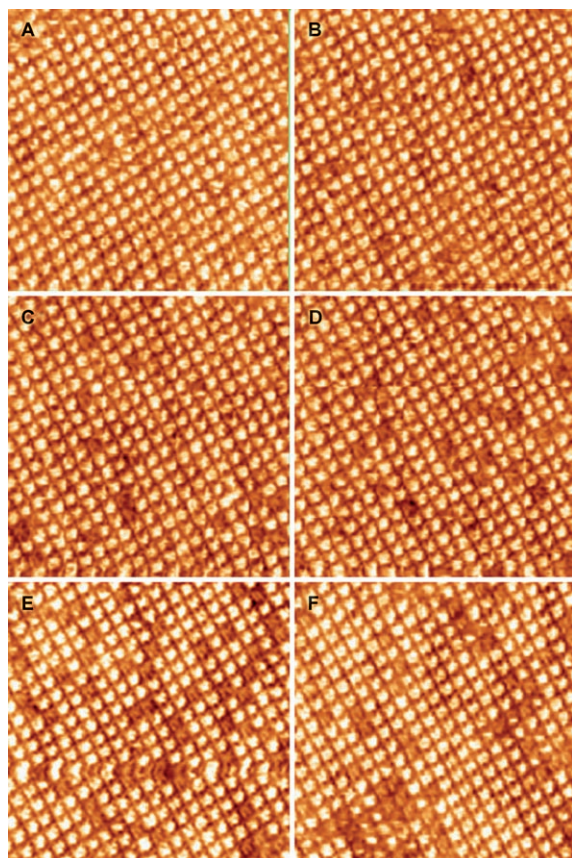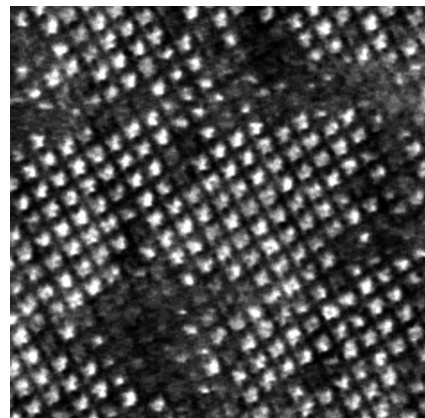

Figure 2. Pre-adsorbed TPyP/Au(111) in 0.1 M H$_2$SO$_4$ at a potential of −0.1 V$_{SCE}$ (27×27 nm^2). A) Before the oxidation potential pulse was applied, and after oxidation of adsorbed TPyP molecules with a potential pulse of 0.2 V for duration: B) 0.1 s, C) 0.2 s, D) 0.5 s, E) 1 s. F) STM image at −0.1 V 3 min after obtaining image (E). Dark spots are oxidized TPyP molecules, light spots are reduced TPyP molecules.

light spots with some apparently randomly distributed dark spots. Each light spot is an adsorbed reduced TPyP molecule.[10] The density of dark spots was found to increase with the duration of the potential-pulse perturbation: the longer the duration of the potential pulse, the higher the density of dark spots. These dark spots can be assumed to be oxidized TPyP molecules and not vacancies for two reasons: 1) our previous studies indicated that the interaction between TPyP molecules and the Au substrate is mainly determined by the electrode potential and the redox state of the adsorbed TPyP molecules; oxidation results in a strong interaction between

TPyP molecules and the Au(111) surface,[10,13] and 2) the dark spots display an internal structure that is characteristic of adsorbed TPyP (see the Supporting Information).

The amplitude of the potential pulse has a significant effect on the dynamics of the TPyP oxidation. The STM image (Figure 3) obtained at −0.1 V after an oxidation potential

Figure 3. Pre-adsorbed TPyP/Au(111) in 0.1 M H$_2$SO$_4$ at a potential of −0.1 V$_{SCE}$ (27×27 nm^2) after oxidation with a potential pulse of 0.3 V$_{SCE}$ for 0.1 s.

pulse of 0.3 V was applied for 0.1 s to the pre-adsorbed TPyP molecules on Au(111) shows that patches, rather than single molecules, of pre-adsorbed TPyP were oxidized. By comparing the surface oxidation reaction after a potential pulse of 0.3 V with that after a potential pulse of 0.2 V, it is clear that a higher oxidation over-potential affects both the oxidation rate and the microscopic nature of the process.

The quantitative analysis of the oxidation dynamics of adsorbed TPyP on Au(111) with potential pulses of different durations and amplitudes is shown in Figure 4. The oxidation rate of the adsorbed monolayer of TPyP on Au(111) was calculated by counting the number of oxidized TPyP molecules after each applied potential pulse. The number of oxidized TPyP molecules on Au(111) is linearly proportional to the duration of the applied potential pulse (Figure 4). Furthermore, higher oxidation potentials apparently increase the oxidation rate of adsorbed TPyP molecules. The data indicates that the oxidation rate of the adsorbed TPyP
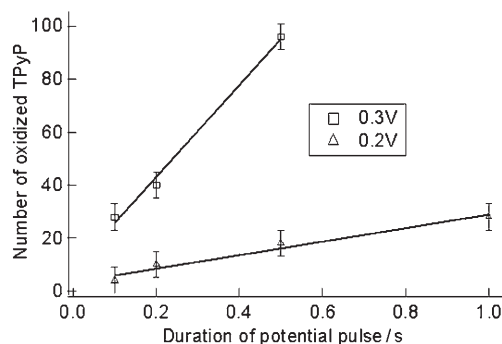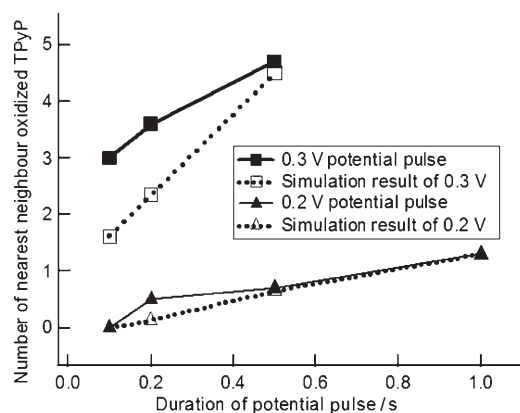

Figure 4. Oxidation of adsorbed TPyP molecules triggered by potential pulses of 0.2 and 0.3 V in a square area (27×27 nm^2).

molecules on Au(111) is $R_{0.2V} = (3.4 \pm 0.4) \times 10^{12}$ molecules cm^{-2} s^{-1} for oxidation pulses of 0.2 V, and $R_{0.3V} = (23.9 \pm 1.8) \times 10^{12}$ molecules cm^{-2} s^{-1} for oxidation pulses of 0.3 V.

By comparing two successive images at -0.1 V potential (Figure 2E,F), we observe that only a small number of TPyP molecules were reduced, and can obtain the reduction rate of oxidized TPyP molecules on Au(111) at this potential. However, the most interesting thing is that the locations of individual oxidized TPyP molecules change. Our previous results show that the interaction between oxidized TPyP molecules and Au(111) is so strong that the mobility of the TPyP molecules on an Au(111) surface is too small to form an ordered monolayer.[10,13] Thus, we suggest that the redistribution of oxidized TPyP molecules results from surface charge diffusion, that is, electron transfer between adsorbed TPyP molecules rather than the physical diffusion (or desorption–re-adsorption) of oxidized TPyP molecules. This result is reminiscent of observations of single-molecule fluorescence "blinking",[7,16] and indicates that the redox state of individual adsorbed molecules on the electrode surface is fluctuating at the single-molecule level.

The k-nearest neighbors analysis method[17] was employed to characterize the distribution of oxidized TPyP molecules. To determine the factors that affect the distribution of oxidized TPyP molecules, we compared the distribution of oxidized TPyP molecules from experiment with the distribution resulting from a Monte Carlo simulation[18] of a completely random arrangement at the same coverage. In the k-nearest neighbors analysis method, the number of oxidized TPyP molecules located around each target oxidized TPyP molecule (Y_i), which reflects how the oxidation of a TPyP molecule affects the probability of the oxidation of neighboring TPyP molecules, was calculated. The average number of oxidized TPyP molecules around each oxidized TPyP molecule was calculated by $Y = \frac{1}{K} \sum_{i=1}^{k} Y_i$, where k is the number of oxidized TPyP molecules in the analyzed area. It is clear that the larger the value of Y, the higher the probability that the neighboring TPyP molecules are oxidized.

The result of the k-nearest neighbor analysis (Figure 5) shows that the oxidation over-potential has a stronger effect than the duration of the potential pulse on the value of Y. For an oxidation potential of 0.2 V, the average value of Y ranges from 0 to 1.3, and the experimental result is in accord with the simulation data, which indicates that the oxidized TPyP molecules are randomly distributed. However, for an oxidation potential of 0.3 V, the distribution of the Y values from experiments (ranging from 3 to 4.7) is larger than that obtained from simulation (from 1.6 to 4.5), assuming a completely random distribution at the same coverages, which suggests that higher oxidation over-potentials result in a clustering of the oxidized TPyP molecules. However, the similarity of the experimental result (4.7) and simulation result (4.5) at longer time (0.5 s) reflects the fact that at high coverages of oxidized TPyP molecules the molecules statistically have a large number of nearest neighbors whether they cluster or not.

The experiments reported here reveal the microscopic details and dynamics of an interfacial oxidation–reduction reaction at the molecular level for the first time. There is significant local spatial heterogeneity at the nanometer scale. A low oxidation over-potential results in a random distribution of oxidized TPyP molecules. Furthermore, the distribution of oxidized TPyP molecules on the Au(111) surface changes with time, thus suggesting that charge diffuses between adsorbed TPyP molecules. A higher over-potential results in oxidation of TPyP patches or domains. This observation provides direct spatially and temporarily resolved insight into interfacial reactions and their dynamics at the single-molecule level. However, this is only an important first step. It is still not clear why the oxidized molecules should tend to form patches at a high over-potential, nor if a threshold potential exists for this process, nor why the distribution of oxidized TPyP molecules on the Au(111) surface changes with time. Also, the present time resolution is limited to relatively slow processes. Using STM with a higher time resolution, for example, video STM,[19] and ultrafast excitation technology[20] may extend the study of single-molecule dynamics to a wider range of timescales.

Figure 5. The spatial distribution of oxidized TPyP molecules as a function of the amplitude and duration of the potential pulse.

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