

Ultrafast Relaxation at Electrochemical Interfaces of Alkanethiol-Modified Gold Electrodes

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Potential dependence of ultrafast electronic responses at Au electrode-solution interfaces was investigated by means of transient reflectivity measurements, in which co-axial pump-and-probe detection was employed with a femtosecond laser and under electrochemical potential control. The interfaces of bare Au(111) and those modified with self-assembled monolayers of 1-dodecanethiol or 1-hexadecanethiol were investigated in aqueous solutions of perchloric or sulfuric acid. A single exponential decay component was observed in each sample system. The decay time constants determined were ranged from 100 to 300 fs and were dependent on the potential, interface modification, and electrolyte in the solution. The interface modification was found to make the decay time constant increase in average as the hydrocarbon chain length increased, although different interfaces had different features of potential dependence. These results are discussed in connection with potential-dependent static and dynamic structures of solvents or adsorbed molecules on the interfaces.

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Electrochemical interface is the region where important catalytic, photochemical, and biological chemical reactions occur. There have been extensive studies on structures or reaction kinetics by several techniques based on conventional electrochemistry, scanning probe microscope, grazing-angle X-ray diffraction, near-edge X-ray absorption fine structure, second harmonic generation, and so on. However, our knowledge about ultrafast interactions at the interface is relatively limited. Chemical reactions at the electrochemical interfaces are dominated by interaction between electrons and molecules, so that most of their elementary processes evolve nonradiatively and in an ultrafast time scale. Understanding of the ultrafast electron dynamics at the interface has fundamental and practical importance for control of these electrochemical reactions such as electrocatalysis or electrosynthesis. Experimental methods that can follow these nonradiative ultrafast processes are required.

Transient reflectivity (TR) measurement is one of the powerful tools that is applicable for observing ultrafast relaxation of electrons at metal surfaces with femtosecond time resolution. Besides, most of research focusing on the ultrafast relaxation process has been performed at solid surfaces in ultra-high vacuum, and little research has been done in bulk liquid and under electrochemical potential control.^{1,2} Experiments in electrochemical systems have some advantages for surface chemistry. They, for example, allow the creation of a wide variety of metal interfaces *in-situ*, and large electric fields may be applied at the metal interfaces, which is not easily achievable in a vacuum. Such experiments can contribute convenience and ease for investigating electron-molecular interactions at the interfaces. At the same time, studying ultrafast relaxation processes at the electrochemical interfaces has a potential to bring understanding to elementary processes of electrochemical reactions.

In this report, we perform femtosecond TR measurements for electrochemical interfaces of single crystalline Au(111) electrodes with/without surface modification by a self-assembled monolayer of alkanethiol in aqueous solutions of perchloric or

sulfuric acid. The electrochemical potential-dependence of TR responses was examined. These results are discussed in connection with potential-dependent static and dynamic structures of solvent or adsorbed molecules on the interfaces.

Experimental

Apparatus

A schematic illustration of the experimental setup is shown in Fig. 1. To investigate the ultrafast response at a single-crystal Au(111) interface in an aqueous-solution, a mode-locked Ti-sapphire laser (Tsunami, Spectra Physics) pumped by an Nd:YVO₄ second harmonic laser (Millennium 5 W, Spectra Physics) was used as a light source. The output light had a pulse width of 80 fs (full width at half maximum of autocorrelation), a wavelength of 800 nm, power of 700 mW, and a repetition rate of 81 MHz. It was divided by a half mirror into two parts for pump-and-probe beams. The pump beam was intensity-modulated at 1.4 MHz with an acousto-optic modulator,

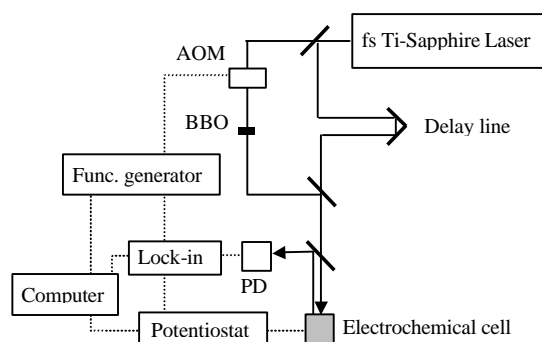


Fig. 1 Schematic illustration of the experimental setup for TR measurements at an electrochemical interface. Some sub-devices are omitted for simplicity.

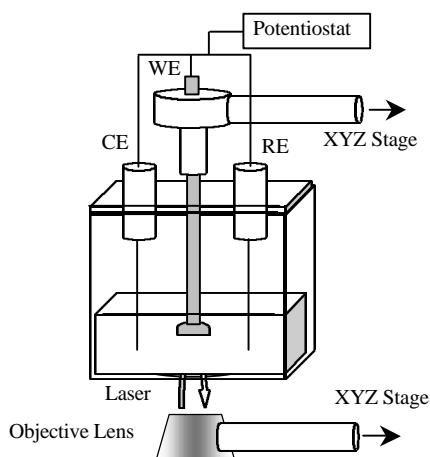


Fig. 2 Electrochemical cell for TR measurements.

transformed to a second harmonic wave (400 nm) by passing through a BBO crystal, focused by a microscope objective lens ($\times 10$), and illuminated normally to the Au/solution interface from the bottom of an electrochemical cell. The fundamental wave was removed before focusing in a pulse-width pre-compensator consisting of a prism pair. The probe beam was coaxially combined with the pump beam before focusing and after passing through an optical delay line. The reflected probe beam from the interface was detected by a photodiode, and its output signal was fed into a lock-in amplifier after passing through a pre-amplifier. The in-phase signal of the lock-in amplifier was recorded as a TR signal with an analog-to-digital converter connected to a computer for further processing. All experiments were performed at room temperature.

Electrochemical cell

A quartz cell was used as the electrochemical cell. The sample of a single crystalline Au served as a working electrode, and two Pt wires were a reference and counter electrodes (Fig.2). The reference electrode of the Pt wire had a potential of 0.7V vs. a standard hydrogen electrode. It was used as a substitution for a generally used reference electrode (i.e., saturated calomel or Ag/AgCl electrode) to avoid disturbing contamination such as Cl⁻. All electrodes were connected to a potentiostat to control the potential of the working electrode. Solution in the electrochemical cell was bubbled with Ar gas to deoxygenate and to maintain cleanliness of the interface during the experiment. The single crystalline Au electrode having a (111) index surface was laboratory-made by Clavilier's method.³

Reagents

Perchloric acid (HClO₄) and sulfuric acid (H₂SO₄) used as solute electrolyte of aqueous solutions were purchased from Kishida Reagents Chemicals and used without further purification. Pure water with 18.2 M Ω cm was systematically prepared by filtration of Milli-Q filter (Millipore system, Japan Millipore Co., Inc.). 1-dodecanethiol (DDT, CH₃(CH₂)₁₁SH) and 1-hexadecanethiol (HDT, CH₃(CH₂)₁₅SH) were purchased from Tokyo Kasei Kogyo Co., Ltd and used without further purification.

Analysis of the TR response

An analysis considering the laser pulse duration was made to obtain time constants of ultrafast relaxations. We assumed that true TR response $R(t)$ was expressed by

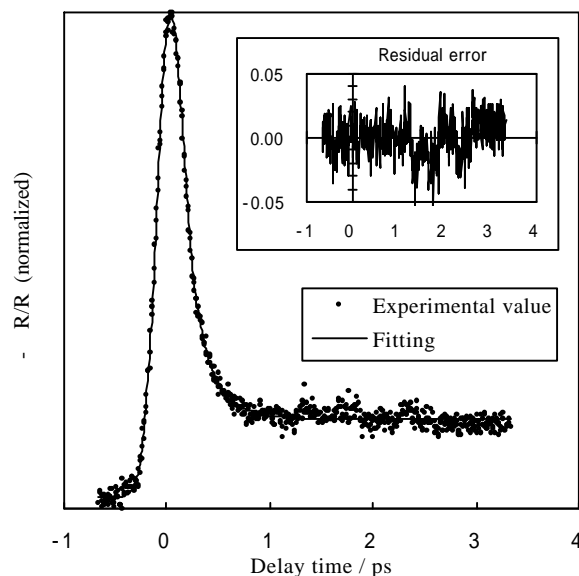


Fig. 3 A fitting result for a TR response at the Au(111) water interface. Note that a ratio of reflectivity decrease ($-\Delta R/R$) is plotted as a function of time. The inset represents the residual error of the fitting procedure. The time constant τ was calculated in 200 fs.

$$R(t) = \sum_{i=1}^n C_i \exp\left(-\frac{t}{\tau_i}\right) + D + d(t) \quad (1)$$

where C_i and τ_i are the pre-exponential factor and the decay time constant of component i , respectively. D and $d(t)$ represent a slow decay component and an instantly responding component, respectively. $R(t)$ is convoluted with a pump pulse intensity profile $I_{\text{pump}}(t)$ and probe pulse intensity profile $I_{\text{probe}}(t)$, where Gaussian pulse shapes are assumed. Thus we obtain $S(t)$ of the fitting function to the experimental data as

$$S(t) = \int_{-\infty}^{\infty} I_{\text{probe}}(t') R(t' - t) \times \left[\int_{-\infty}^{t'} I_{\text{pump}}(t'') R(t' - t'') dt'' \right] dt' \quad (2)$$

It has been reported that bi- or tri-exponential function is enough for fitting to TR responses of Pt in solutions observed during initial 4 ps.¹ We found single exponential function with D and $d(t)$ provided good fitting results for measured responses, as shown in Fig.3.

The decay time constants calculated were in a sub-picosecond time scale. The relaxation at that time was considered to be caused by electron-electron and electron-phonon couplings at the interface. A cross-correlation calculation of the pump-and-probe beams had 240 fs of full width at half maximum. It was small enough to determine decay time constants of hundreds of femtoseconds.

Results and discussion

Cyclic voltammetry

Cyclic voltammograms of Au(111) and DDT-modified Au(111) in a 0.1 M HClO₄ aqueous solution are shown in Fig. 4. For the Au(111) interface, two oxidation peaks owing to Au hydroxide formation were observed at 0.5 and 0.75 V vs. Pt in the anodic sweep, and one reduction peak was at 0.3V vs. Pt in the cathodic sweep. These featured a (111) index surface of Au in HClO₄.⁴

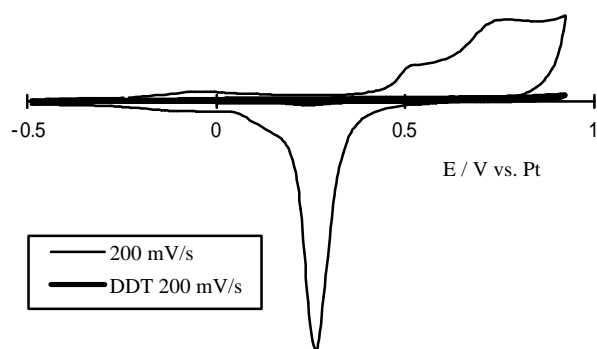


Fig. 4 Cyclic voltammograms of Au(111) and 1-dodecanethiol (DDT)-modified Au(111) in 0.1 M HClO_4 . The sweep rate was 200 mV/s.

When Au was modified with DDT, these oxidation or reduction peaks disappeared. Electrochemical inertness of an alkanethiol adlayer at the interface was confirmed. A similar cyclic voltammogram was observed for an HDT-modified Au(111).

Decay time constants for an Au(111) in an HClO_4 aqueous solution

A series of decay time constants against the electrode potential for each system at the Au(111) interface in a 0.1 M HClO_4 aqueous solution is shown in Fig. 5. Three different systems were examined that included bare Au(111), DDT-modified Au(111), and HDT-modified Au(111). We, first of all, found interface modification resulted in slow relaxation. The decay time constants averaged over the potential range from -0.5 to 0.75 V vs. Pt were 120, 160, and 260 fs for bare, DDT-modified and HDT-modified Au(111) interfaces in the HClO_4 solution, respectively. The time constants increased with an increasing hydrocarbon chain length. For the bare Au(111) interface, it was observed that the time constant increased in the potential range of 0.2–0.6 V vs. Pt. More remarkable dependencies were observed both for the DDT-modified and HDT-modified Au(111) interfaces, in spite of electrochemical inertness at the interfaces. The potential ranges where decay time constants were large shifted to negative potentials. They were 0.2–0.6 V vs. Pt, 0.1–0.3 V vs. Pt, and -0.2–0.2 V vs. Pt for bare, DDT-modified and HDT-modified Au(111) interfaces, respectively.

For the bare Au interface, it might be considered that the potential dependence came from Au oxide and hydroxide formation at the interface because the potential range of the increase in decay time was overlapped with the oxidation and reduction potentials of Au as seen in the cyclic voltammogram. However, this oxidation mechanism gave no explanation for potential dependence at the low potentials. Moreover, it is not applicable for the modified Au interfaces because it has been known that an alkanethiol adlayer prevents oxidation and reduction reactions on the Au interface. We considered that interfacial changes that had resulted from oxidation-reduction reactions were not major reasons for varying the decay time constants.

One possible explanation of the potential dependence was the change in static and dynamic structure of the molecular assembly at the interface. We can suppose that some electron transfer and back transfer between the metal and molecules (or ions) on the interface take place in an ultrashort time or image dipoles caused by molecular dipoles interact with excited electrons in metal. For polarizable interfaces, structure of molecular assembly at the solution side of the interface depends on the potential. It is known that for a bare Au interface, a dipole moment of water changes its direction with the potential, while the mean distance of water molecules from the Au changes at the same time. A stretching vibration of OH has such a high

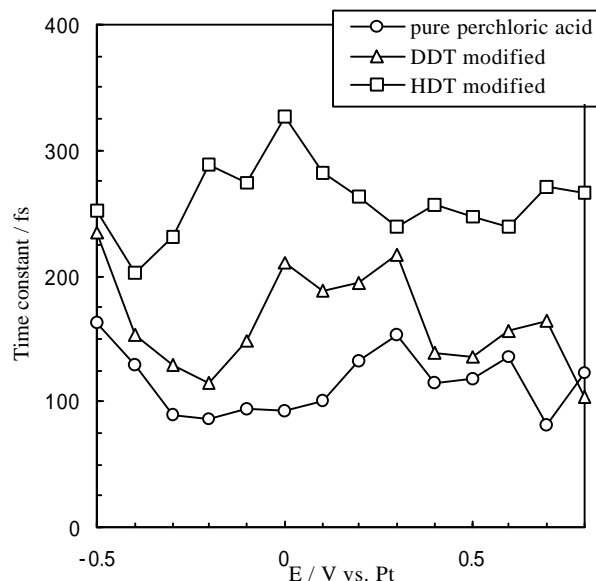


Fig. 5 Potential dependence of decay time constants at the Au(111) interface in a 0.1 M HClO_4 aqueous solution.

frequency that it could couple with electron motions in the metal during hundred of femtoseconds.

For the modified interfaces, a stretching vibration of CH has a frequency that is high enough for the coupling, and a change in tilt angles of the alkanethiol molecules in their adlayer may cause the time constant change. It could be supposed that the transition of the binding site from a hollow to the top of an Au atom occurred against the potential at the interface.

Potential-sweep experiments

We performed the potential-sweep experiments because the long time measurements that are required to obtain potential-dependent decay times, which are shown in Fig. 5, are likely to result in some systematic errors due to the instability of experimental setup. The potential dependence of ultrafast relaxation processes was confirmed by the experiments. Figure 6 represents the results for the DDT modified Au(111) interface in a 0.1 M HClO_4 aqueous solution. Correspondence between a TR response (left) and TR intensity against the potential at each delay time (right) is shown. The potential-dependent TR response had a different slope, especially in the range of 0.2–0.5 V vs. Pt, depending on the delay times. This means that the decay time depends on the potential. We confirmed the potential dependence of the decay time constants for the other interfaces in an aqueous solution of 1.0M HClO_4 or 0.1M H_2SO_4 .

Decay time constants for the Au(111) in an H_2SO_4 aqueous solution

The TR measurements were preliminarily performed at the Au(111) interfaces in the H_2SO_4 aqueous solution to compare with the results of the Au(111) interface in the HClO_4 aqueous solution. The potential dependence of the decay time constants was also observed, however, the extent of the potential dependence was smaller, and its potential range was broader than those for Au in HClO_4 aqueous solution. The decay time constants, which averaged over the potential range from -0.5 to 0.75 V vs Pt, were 220, 220, and 230 fs for bare, DDT-modified, and HDT-modified Au(111) interfaces, respectively. Potential ranges where time constants took large values showed no substantial change by interface modification. Table 1 summarizes these results together with results for the HClO_4 aqueous solution.

These results lead us to believe that the solute anion SO_4^{2-} rather than the alkanethiol adlayer played an important role in

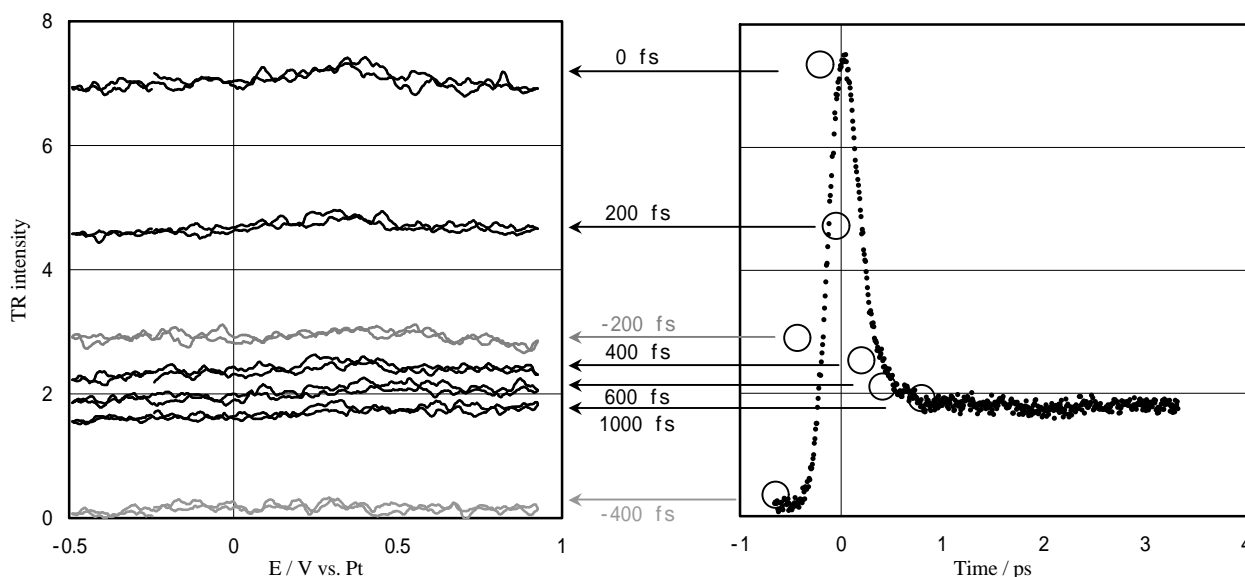


Fig.6 Results of potential-sweep experiments at each delay time (left); TR intensity against potential at each delay time is shown with the corresponding time in the TR response (right). Notice that the inverse value of the TR intensity ($-\Delta R/R$) is represented with an arbitrary unit.

Table 1 Average values of decay time constants at the measured potential range and potential ranges for an increase of time constants.

Solution	Decay time constants (fs)			Potential range (V vs. Pt)		
	Bare-Au	DDT-Au	HDT-Au	Bare-Au	DDT-Au	HDT-Au
Perchloric acid, 0.1M	120	160	260	0.2 ~ 0.6	-0.1 ~ 0.3	-0.2 ~ 0.2
Sulfuric acid, 0.1M	220	220	230	0.3 ~ 0.5	-0.1 ~ 0.3	0.2 ~ 0.5

determining the decay time constants at the Au(111) interfaces. It was surprising that time constants were dominated by SO_4^{2-} anions for the modified Au interfaces because the adlayer blocks anions. Different dependencies between the HClO_4 and H_2SO_4 systems were considered to come from difference in interfacial species having a different affinity to the Au interface or alkanethiol molecules. The strong affinity could cause a small potential dependence for the bare Au interface. The stronger affinity of SO_4^{2-} over ClO_4^- is known for Au interface, although it is unknown for alkanethiol molecules. These speculations above must be confirmed by several TR measurements by use of other solutions and alkanethiols.

Conclusion

Potential dependence of femtosecond TR responses was measured for bare and modified Au(111) interfaces in an aqueous solution of HClO_4 or H_2SO_4 . The decay time constants determined were ranged from 100 to 300 fs and were dependent on the potential, interface modification, and electrolyte in the solution. We found that interface modification makes the decay time constant increase as the hydrocarbon chain length increases, and different interfaces had different features of potential dependence. When an H_2SO_4 solution was used, no substantial modification effect was observed, while decay time constants depended on the potential. These results are discussed in connection with the potential-dependent static and dynamic structures of solvents or adsorbed molecules on the interfaces. It was speculated that the different dependence of time constants between the HClO_4 and H_2SO_4 systems originated from different interfacial structure caused by interfacial species.

A combination of femtosecond TR measurements with electrochemistry is now being developed. We expect it to give temporal and energetic information about relaxation of electrons occurring at the electrode-solution interface. Structural information of the interface should be the most important. However, we believe that our trial can open a pathway to an undeveloped region in electrochemistry from the standpoint of ultrafast charge transfer and ultrafast energy flow through the interface.

Acknowledgements

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