Femtosecond Time-Resolved Transient Reflectivity at the Au(111) Electrode/Aqueous Solution Interfaces.   The Effects of Laser Photon Impact, Electrochemical Potential Control, and Modification by Alkanethiols.

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Femtosecond transient reflectivity (TR) was measured at electrochemical interfaces to discuss ultrafast elementary processes of electrochemical phenomena.   A pump and probe technique was employed to measure TR at the interface using a femtosecond Ti-sapphire laser.   An Au(111) electrode interface and one modified with a self-assembled monolayer of alkanethiols were studied under an electrochemical potential control.   A solute of $HClO_4$ or H_2SO_4 was used as a supporting electrolyte of aqueous solutions.   An ultrafast decaying component of subpicoseconds, an instantly responding component and a long-lived component were observed in a TR response.   It was found that the decay rate constant of the decaying component depended on electrochemical potential and interfacial modification.   The rate constants for 1-octanethiol-modified Au were smaller than that for an unmodified Au in an aqueous $HClO_4$ solution.   A small but certain dependence of the rate on the electrochemical potential was observed even at the electrochemically inert interface.   These results are discussed in terms of interfacial molecular structure at aqueous solution side of the interface.

Recently, spectroscopic measurements using femtosecond lasers brought us important information about electron dynamics in molecules and materials with a time-resolution of femtoseconds.[1-3]   The study of ultrafast energy transfer at a metal surface has potential not only to open pass way into the novel chemical reaction,[4] but also to elucidate interface-intrinsic chemical reactions between a substrate and an adsorbed-molecule such as catalytic reactions at a material surface and electrochemical reactions at an electrode interface. When light illuminates a metal surface, excited electrons are generated in the metal and interact with adsorbed-molecules, that takes place in a time scale of picosecond for most of metal surfaces.   This ultrafast interaction can dominate final chemical products and final energy redistribution.

An electrochemical interface of a metal electrode/liquid interface is one of the ideal systems for study of the ultrafast processes, because the state of adsorbed-molecule can be easily controlled *in-situ* by the electrochemical potential of the electrode.   It is expected that development of the ultrafast study at the electrochemical interface will advance electrochemistry, catalytic chemistry and surface chemistry, but there are very few reports.[5-6]

Transient reflectivity (TR) measurements are useful methods for observation of electron dynamics at metal surfaces,[7-8] and applicable to the solid(metal)/liquid interface.   We have applied a TR measurement at an Au(111) electrode/aqueous solution interface and reported that a TR decay at the interface depended on the electrochemical potential of the electrode and interfacial molecular structure.[9]

In this paper, we report results of TR measurements at a 1-octanethiol (OT, $CH_3(CH_2)_7SH$) modified Au(111) interface in an aqueous solution.   Alkanethiols form self-assembled monolayer (SAM) on Au surface with Au-S chemical bond.[10] We examine the effect of hydrophobic environment by SAM upon a TR response in a time scale of a few picoseconds. Electrochemical potential dependence of a TR response is examined at the OT-modified interface.

Experimental

Apparatus

The same experimental setup as previously reported was used.[9]   Pump and probe beams delivered from a mode-locked Ti-sapphire laser.   The probe beam had a pulse width of 80 fs (full width at half maximum of autocorrelation), a wavelength of 800 nm (1.6 eV), a repetition rate of 81 MHz and was passed through an optical delay line.   The pump beam was intensity-modulated at 1.4 MHz and its wavelength was transformed into a second harmonic wave at 400 nm (3.1 eV). Coaxially combined two beams were focused by a plano-convex lens with a microscope objective lens (magnification, 10; numerical aperture, 0.25) and normally directed into an electrochemical interface.   The powers of pump and probe beams were less than 160 and 300 pJ/pulse at the interface, respectively.

Electrochemical cell

A hemisphere electrode of a single crystalline Au having a (111)-index surface was modified with OT by immersing in a 1 mM ethanolic OT solution for more than 24 hours.   The electrochemical cell was consisted of a three electrodes configuration.   The OT-modified Au(111) was served as a working electrode, and two Pt wires were a reference and
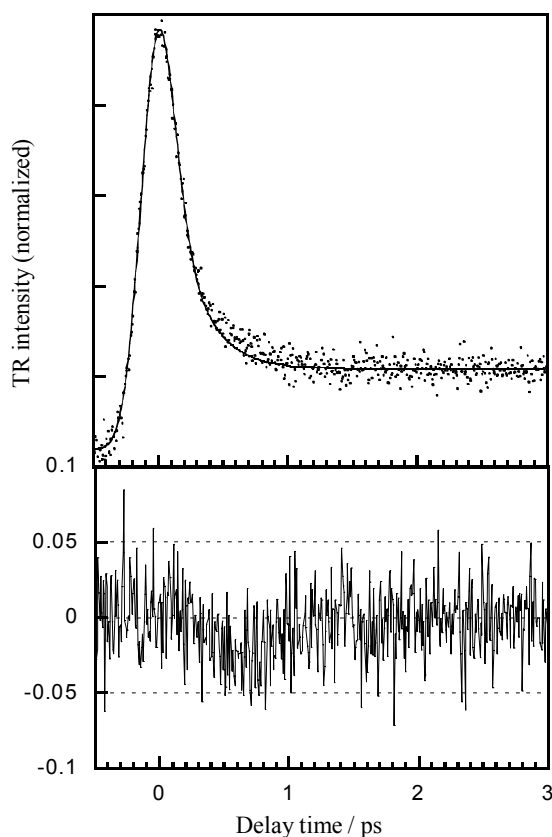
Fig. 1 Upper: TR response at 0.4 V (dot) and fitting line at −0.5 V (solid line) at the 1-octanethiol-modified Au(111) interface in a 0.1 M aqueous $HClO_4$ solution, each data was normalized. Lower: difference between them.

counter electrodes. The Pt reference electrode had an electrochemical potential of 0.7 V versus the 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 by Cl⁻. A solution in the electrochemical cell was bubbled with Ar gas to deoxygenate and to maintain cleanliness of the interface during the experiment.

Reagents

$HClO_4$ and H_2SO_4 were purchased from Kishida Reagents Chemicals and used without further purification. Those were used as a solute electrolyte of aqueous solutions after dilution. Pure water with 18.2 MΩcm was systematically prepared by filtration of Milli-Q filter (Millipore system, Japan Millipore Co., Inc.). 1-octanethiol (OT, $CH_3(CH_2)_7SH$) were purchased from Tokyo Kasei Kogyo Co., Ltd, and were used without further purification.

All experiments were performed at room temperature at atmospheric pressure.

Results and Discussion

It has already been reported that decay time constants of a TR depended on the electrochemical potential at the Au(111) interface in a 0.1 M aqueous $HClO_4$ solution.[9] It was considered that the electrochemical potential dependence of time constants was due to the rearrangement of water dipole that occurred around 0.2 V vs Pt at the Au(111)/$HClO_4$ aqueous
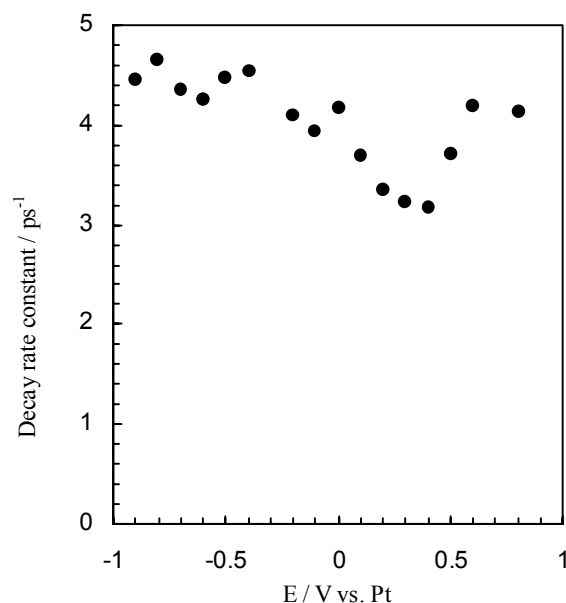

Fig. 2 Electrochemical potential dependence of decay rate constants at 1-octanethiol-modified Au(111) interface in 0.1 M aqueous $HClO_4$ solution.

solution interface. Potential dependence is expected to disappear when an Au electrode is modified with an alkanethiol because of hydrophobic environment and electrochemical inertness at the interface. However, what was actually observed for an Au electrode in an aqueous $HClO_4$ solution was the potential dependence of the decay time constants remained even when the electrode was modified with 1-dodecanethiol or 1-hexadecanethiol.[9] When the Au(111) interface is modified with OT having a shorter hydrocarbon chain than 1-dodecanethiol and 1-hexadecanethiol, a similar but large dependence is expected.

Analysis of a TR response

A decay rate constant, k, is calculated from a TR response although our group has reported a decay time constant ($=1/k$) in a previous report.[9] A true TR response, $R(t)$, is rewritten as

$$R(t) = C \cdot \exp(-k \cdot t) + D + \delta(t) \qquad (1),$$

where C, D and $\delta(t)$ are the pre-exponential factor, a slow decay component and an instantly responding component, respectively. Gaussian pulse shapes of pump and probe pulses are convoluted to eq. (1), giving a fitting function for TR response.

A TR at the OT-modified interface in an aqueous $HClO_4$ solution

A TR response within 3 ps of a delay time at the OT-modified interface in an aqueous $HClO_4$ solution is shown in the upper part of Fig. 1. At the electrochemical potential of 0 vs Pt, a decay rate constant of 4.2 ps⁻¹ was obtained at the OT-modified interface. This value is smaller than 10 ps⁻¹ corresponding to the decay time constant of 93 fs observed at an unmodified Au(111) interface. Electrochemical potential dependence of the decay rate constant was observed at the OT-modified interface. Figure 1 shows deference between TR responses at −0.5 and 0.4 V vs Pt. A solid line and dots in upper part represent the fitting result for a TR response measured at −0.5 V vs Pt and the row data of a TR response measured at 0.4 V vs Pt, respectively. The lower part shows difference between them. As seen in Fig. 1, difference between them is quite small.
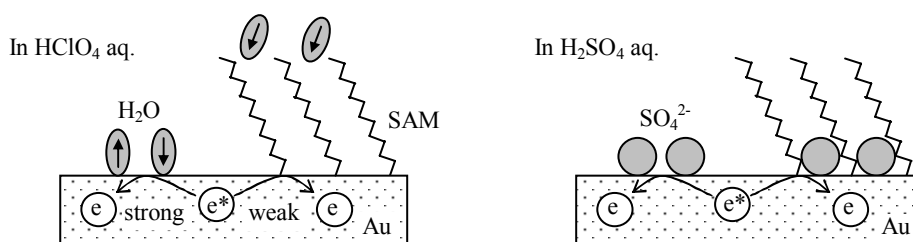
Fig. 3 Schematic illustration of ultrafast relaxation models at the Au(111) electrode interface. e, e* represent electrons and electrons with photo-induced large energy, respectively. An arrow in H_2O corresponds to direction of its dipole.

However, systematic deviation shown as the difference especially around 0.5 ps of delay time apparently indicate existence of potential dependence. Decay rate constants calculated are 4.5 ps^{-1} at –0.5 V vs Pt and 3.2 ps^{-1} at 0.4 V vs Pt, respectively. It is confirmed that a decay rate constant depends on the electrochemical potential at the OT-modified interface.

A series of rate constants determined against the electrode potential at the Au(111) interface modified with OT in an aqueous $HClO_4$ solution is shown in Fig. 2. It is clearly observed that decay rate constants depend on the electrochemical potential and have a minimum around 0.2 ~ 0.4 V vs Pt. An averaged value of rate constants is 4.2 ps^{-1} at the OT-modified interface in a measured potential range from –0.9 to 0.8 V vs Pt. On the other hand, an averaged value of decay rate constants was 9.4 ps^{-1} at the unmodified interface in a measured potential range from –0.3 to 0.8 V vs Pt. Apparently interfacial modification reduces decay rate constants in an aqueous $HClO_4$ solution.

The cause of the TR signal at the interface is considered as photo-induced change in the complex refractive index by a population change of electrons in the conduction band of Au. Electrons with large energy after photoexcitation are called nonequilibrium electrons. The ultrafast decay of TR comes from relaxation of the photo-induced nonequilibrium electrons by diffusion of the electrons and electron-phonon coupling at the photo-illuminated interface. The decay rate constant calculated in this study correlates with the rate constant of the nonequilibrium electron relaxation, because of the time scale in sub-ps. It is natural to suppose that interaction of nonequilibrium electrons in metal with adsorbed-molecule dominates the decay rate constant and causes the potential dependence. We think rearrangement of water dipole is the cause of the potential dependence at the unmodified interface. Results of modification with alkanethiols suggested reducing interaction between nonequilibrium electrons in Au and surrounding environments. It is considered that the decrease of decay rate constant by modification is due to taking water molecules apart from the interface. On the other hand, it is interesting that potential dependence remained even when the interface was modified. Potential-induced change in the interface electron density is one of possible explanations. If the relaxation rate of nonequilibrium electron is simply proportional to the charge density in Au, a linear relation is expected between the decay rate constant and the electrochemical potential. This was not the case. Some structural change of OT in SAM may be one of the best candidates.

A TR at the OT-modified interface in an aqueous H_2SO_4 solution

When an aqueous H_2SO_4 solution was used, no substantial modification effect as seen in an aqueous $HClO_4$ solution was observed, while rate constants depended a little on the potential. The averaged value of the rate constants is 4.7 ps^{-1} at the OT-modified interface and 5.1 ps^{-1} at the unmodified interface in a potential range from –0.4 to 0.7 V vs Pt. This result is similar with those of modification with 1-dodecanethiol and 1-hexadecanothiol.[9] It is considered that the small potential dependence is caused by SO_4^{2-} for the unmodified interface because of the stronger affinity of SO_4^{2-} to Au than ClO_4^-.[9] The small effect of modification may have the same origin but it is not clear at the present stage.

Summary

Figure 3 schematically illustrates ultrafast relaxation of nonequilibrium electrons in Au. In an aqueous $HClO_4$ solution, water dipole plays an important role in relaxation of photo-induced nonequilibrium electrons and SAM represses the relaxation, which results in a slow decay of TR. On the other hand, SAM doesn't affect the relaxation of TR at the interfaces in an H_2SO_4 aqueous solution, for which the stronger affinity of SO_4^{2-} to Au may concern.

Acknowledgement

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