

Ultraslow relaxation of the structure at the ionic liquid|gold electrode interface to a potential step probed by electrochemical surface plasmon resonance measurements: asymmetry of the relaxation time to the potential-step direction

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[Abstract]

The relaxation of the structure in the electrical double layer at the ionic liquid|gold interface to the steps of the electrode potential has been studied using surface plasmon resonance (SPR) measurements. The relaxation of the SPR resonance angle occurs on the order of 100 s, which is distinctively slower than the RC time constant of the cell, about 0.1 s. A relaxation model considering the distribution of the time constants well reproduce the SPR curves. The potential steps to the positive direction lead two order of magnitude slower relaxation of the SPR resonance angle than those to the negative direction. The ultraslow relaxation and its asymmetry to the potential-step directions are likely to be caused by slow inter-layer dynamics of ions in the ionic multilayers and interaction of ions with gold, respectively.

Recently we reported ultraslow relaxation of the structure in the electrical double layer (EDL) to the change in the phase-boundary potential at the electrochemical interface between hydrophobic ionic liquid (IL) and water (W).¹⁻⁴ The potential-step measurements,² revealed that both the surface tension at and the charging current across the IL|W interface show the ultraslow relaxation with time constants on the order of 10 s. The time constants of the ultraslow relaxation depend on the ionic species constituting the hydrophobic ILs but are not correlated with the bulk viscosity of the hydrophobic ILs.⁴ The results suggest that dynamics of IL-constituting ions in the EDL at the IL|W interface is unexpectedly slow compared with that in bulk.

For the IL|metal interface, long-time hysteresis has been reported for the capacitance⁵⁻⁸ and the orientation of ions.⁹ Recently we also found ultraslow relaxation at the IL|Pt interface, similar to that at the IL|water interface, by using potential step chronoamperometry and cyclic voltammetry.¹⁰ The fact that the two electrochemical interfaces of ILs show the ultraslow relaxation suggests that the major reason of the ultraslow relaxation is not the interaction of the IL-constituent ions with water or metal surface, but the collective rearrangement of the ions in the EDL at the IL side of the interface,^{1-4,10} where ionic multilayers have been found to be formed.¹¹⁻¹⁸ Drüscher and coworkers also reported slow process occurring at the IL|Au(111) interface by using electrochemical impedance spectroscopy (EIS).^{19,20} In the complex capacitance plots from the EIS measurements, they found the second slower arc having a time scale of second, in addition to the usual *RC* charging arc.

In the study on the ultraslow relaxation at the IL|metal interface described above,^{10,19,20} current was used to probe the rate of the change in the EDL structure. The current becomes more sensitive to the change when the relaxation is fast. We found ultraslow relaxation on the order of seconds at the IL|Pt interface using current as a probe.¹⁰ Therefore, in order to detect possible relaxation of the EDL structure slower than seconds with a high sensitivity, another probe that can reflect not the EDL change but the EDL structure would be valuable. In the present study we employed the electrochemical surface plasmon resonance (ESPR)^{21,22} to investigate the ultraslow relaxation at the IL|gold interface. ESPR has been used to characterize the properties of films at the electrode surface in response to the change of electrode potentials,²³⁻²⁷ and monitor redox reaction of small molecules^{28,29} and enzymes³⁰⁻³² at electrode surfaces. An ESPR study of the interface between gold and an aqueous solution of IL, added as an electrolyte, has also been recently reported.³³ In this letter, we will show ultraslow relaxation on the order of 100 s at the IL|gold interface and the asymmetry of the relaxation time to the potential-step directions.

Triocetyltrimethylammonium bis(nonafluorobutanesulfonyl)amide ([TOMA⁺][C₄F₉N⁻]) was used as IL. The IL was prepared and purified using the same method as that previously described.¹ ESPR measurements were performed using a SPR apparatus (Springle, Autolab) with a Kretschmann configuration.³⁴ The IL was filled in a three-electrode ESPR cell. The bottom of the ESPR cell is a gold film (50 nm thickness), which was prepared by vapor deposition on one side of a glass slide of SF15 with a refractive index, *n*, of 1.6911 at 670 nm. The other side of the glass slide was attached to the flat surface of a hemicylindrical prism made of SF15 glass with an immersion oil (*n*=1.698 at 589 nm, Cargille Labs.). p-polarized light with a wavelength of 670

nm was irradiated to the gold|SF15 interface from the convex surface of the hemicylindrical prism, to excite the surface plasmon polariton at the IL|gold interface. The surface area of the gold film as a working electrode was 0.080 cm². A Ag wire coated with AgCl was directly immersed in the IL as a quasi-reference electrode, and a Pt wire as a counter electrode. The potential of the gold film electrode with respect to the Ag/AgCl electrode, denoted as E , was controlled using a PC-controlled potentiostat (Autolab type III). Before measurements, IL was pumped for more than 6 h at 50 °C by a rotary oil pump. The mass fraction of the water content in the IL measured using Karl Fischer coulometry was typically lower than 0.0001. During measurements, water from a temperature-controlled bath with the temperature of 25.0 °C was kept flowing in the jacket of the cell and Ar gas (99.9%) was kept flowing over the surface of the IL. Time variation of surface plasmon resonance angle, $\theta_{\min}$, which is defined as the incident angle where the reflectivity becomes minimum due to SPR, was monitored.

Figure 1a shows a cyclic voltammogram at the [TOMA⁺][C₄C₄N⁻]|gold interface. Only capacitive current flowed across the interface in the potential region between -0.3 V and +1.1 V with a width of 1.4 V. In this study, we conducted ESPR measurements within this capacitive potential region shown in Fig.1a. Fig. 1c shows a time variation of $\Delta\theta_{\min}$ when the multiple potential step sequence shown in Fig.1b was applied. When the potential was stepped from -0.3 to +0.7 V at $t = 0$ s, $\Delta\theta_{\min}$ at first jumped from 0 to -25 mdeg. The transition time for this fast change in $\Delta\theta_{\min}$ was not able to be measured because it was faster than the sampling interval of the present measurements, 0.5 s. After the initial jump, $\Delta\theta_{\min}$ slowly relaxed from -25 to +10 mdeg. For the negative potential step from +0.7 to -0.3 V at $t = 300$ s, $\Delta\theta_{\min}$ shifted to the positive direction and slowly decayed to the negative direction. The initial jump is probably not ascribable to the charging process, in which cations and anions collectively move in a opposite way along with surface normal. Although the origin of the jump is not clear, the polarization relaxation such as electronic and orientational polarization of ions at the bottommost ionic layer next to the gold surface would change the refractive index distribution at the interface. In fact, the potential dependence of the ionic orientation at IL|electrode interface has been reported in several studies using surface spectroscopic techniques³⁵⁻³⁸ and molecular dynamics simulation (MD).³⁹⁻⁴⁴

After the initial jump, Fig.1c shows slow relaxation of $\Delta\theta_{\min}$ for both of positive and negative potential steps on the order of 100 s. This time scale is significantly slower than the RC constant of the present cell estimated from the solution resistance and the electrode capacitance, which is on the order of 0.1 s. Such an anomalously slow relaxation, which has not been observed in previous ESPR studies on the molecular solvent|electrode interfaces,^{45,46} reflects the uniqueness in the structure and structural change of the EDL in ILs. It is noted that current response, which was simultaneously monitored in the ESPR measurements, showed faster (but still slower than the RC constant) response than $\Delta\theta_{\min}$ (Fig.S2), indicating that ESPR is suitable to track the slower components of the ultraslow relaxation of the EDL structure. The slow $\Delta\theta_{\min}$ change is likely to originate from two contributions: the n change at the topmost gold layer due to the change in the surface charge density and the n change in the EDL where the distribution of ions is different from that in bulk. We estimated the two contributions are comparable judging from the calculation⁴⁷ by using the McIntyre model^{48,49} for the

former contribution and the EDL models of ILs such as the Oldham's one⁵⁰ for the latter contribution.

Moreover, Fig.1c shows a difference in the shape of the relaxation curves for the positive and negative potential steps. The relaxation time for the positive steps is significantly slower than that for the negative steps. Such a significant step-direction difference in the relaxation time has not been observed in the previous studies on the ultraslow relaxation of the electrochemical IL interfaces.^{1-4, 10} To quantitatively analyze the time scale of the ultraslow relaxation, the relaxation curves of $\Delta\theta_{\min}$ were fitted with model functions. Figure 2 shows the fitting results to the experimental relaxation curves for the positive potential step ($0 \leq t/s \leq 300$) and the negative potential step ($300 \leq t/s \leq 600$) as examples. The single exponential relaxation function ($e^{-t/\tau}$), which is one of the simplest models for the relaxation, failed to reproduce the experimental relaxation curves (dotted lines in Fig. 2). Such failure for the single exponential function to model the ultraslow relaxation has already been found in our previous studies, where we used two exponential relaxation function instead for the analysis of the ultraslow relaxation.^{2, 10} In this study, we used a digitized form of a log normal distribution function since it has the number of fitting parameters, four, smaller than that for the double exponential function, five, and it showed smaller AIC (Akaike's Information Criterion, a measure of likelihood of models) values in the fitting. The log normal distribution function, $P'(\log \tau_i)$, may be expressed as^{51, 52}

$$P'(\log \tau_i) = \frac{\exp\left\{-\frac{(\log \tau_i - \log \tau_0)^2}{2\sigma^2}\right\}}{\sum_{i=1}^{i_{\max}} \exp\left\{-\frac{(\log \tau_i - \log \tau_0)^2}{2\sigma^2}\right\}} \quad (1)$$

$$\log \tau_i = \log \tau_{\min} + \frac{i-1}{i_{\max}-1} (\log \tau_{\max} - \log \tau_{\min}) \quad (2)$$

where $\log \tau_0$ and σ are the mean and the standard deviation of the distribution, respectively, and $i_{\max}$ is the total number of the digitized discrete time constants, τ_i . The model function for the $\Delta\theta$ relaxation becomes

$$\Delta\theta(t) = \Delta\theta(t_{\text{step}}) + \Delta\theta_{\text{fast}} u(t_{\text{step}}) + \Delta\theta_{\text{slow}} \sum_{i=1}^{i_{\max}} P'(\log \tau_i) \left\{1 - \exp\left(-\frac{t - t_{\text{step}}}{\tau_i}\right)\right\} \quad (t \geq t_{\text{step}}) \quad (3)$$

where $\Delta\theta(t_{\text{step}})$ is $\Delta\theta(t)$ just before the potential step at $t = t_{\text{step}}$, $\Delta\theta_{\text{fast}}$ and $\Delta\theta_{\text{slow}}$ are the fast and slow components of the change in $\Delta\theta(t)$ after the step, respectively, and $u(t)$ is the unit step function. Eq 3 was used for the fitting to the experimental curves with four variable parameters ($\log \tau_0, \sigma, \Delta\theta_{\text{fast}}, \Delta\theta_{\text{slow}}$) and other fixed parameters. The fixed parameters are $\log(\tau_{\min}/s) = -3$, $\log(\tau_{\max}/s) = +6$, and $i_{\max} = 180$. Examples of the fitting results are shown in Fig.2a as black dashed lines. The fitted curves well reproduced the experimental data. The parameters obtained by the fitting are listed in Table 1. The values for $\log(\tau_0/s)$ for the positive and negative steps are 2.40 and 0.29, respectively. The two order of magnitude difference in τ_0 clearly shows the asymmetry of the relaxation time to the potential-step direction (Fig.2b). Both of the time constants are significantly greater than the order of sub-seconds, those obtained by us at IL|Pt interface using current as a probe.¹⁰ This significant difference is likely to be due to the probe; current senses the rate of the change in EDL and has a high sensitivity for fast response, while ESPR signal reflects the structure of EDL and has a high sensitivity for slow response. The σ values for the positive and negative steps are similar to each other (1.23 and 1.08),

indicating that the relaxation process has a distribution of time constant over the range of orders regardless of the potential-step direction (Fig. 2b). The absolute values of the fast and slow components, $|\Delta\theta_{\text{fast}}|$ and $|\Delta\theta_{\text{slow}}|$, for the positive step, 61 and 40 mdeg., is greater than those for the negative step, 44 and 31 mdeg., respectively. This probably results from the incompleteness of the two-order-slower relaxation for the positive step when the next negative step is performed (at $t = 300, 900, 1500$ s).

A question is how the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ gold interface is charged when the potential is set at +0.7 and -0.3 V. An important parameter to tackle this question is the potential of zero charge (E_{pzc}) of the interface. We measured E_{pzc} of the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ gold interface by using the immersion method.⁵³⁻⁵⁷ The E_{pzc} value was evaluated to be +0.5 V vs. Ag/AgCl quasi-reference electrode (+0.1 V vs. ferrocene/ferricinium redox reference).⁵⁸ Therefore, at $E = +0.7$ V, which is close to E_{pzc} , the gold surface is likely to be slightly positively charged. The number of anions at the IL side of the interface is almost the same as that of cations. On the other hand, at $E = -0.3$ V, the gold surface is negatively charged, and cations (anions) are accumulated (depleted) at the IL side of the interface. We measured potential-step transients of $\Delta\theta_{\text{min}}$ at two different potential sets, (+0.9, -0.1 V) and (+1.1, +0.1 V) by keeping a step width of 1 V. The sequence of the relaxation curves are shown in Figs.S2 and S3, and the fitted parameters are listed in Table 1. The values for $|\Delta\theta_{\text{fast}}|$ and $|\Delta\theta_{\text{slow}}|$ becomes smaller for more positive potentials. In a SPR study for metal|aqueous solution interface the dependence of $\Delta\theta_{\text{min}}$ at equilibrium on the potential and ionic species in the solution was found,⁵⁹ and the dependence was attributed to several factors such as the charged state of the electrode and the EDL structure. The τ_0 values on the potential seem larger for more positive potentials, which probably also reflect the several factors. The most important point in Table 1 is the asymmetry; the asymmetry of the relaxation times found for the (+0.7, -0.3 V) step is also apparent for the (+0.9, -0.1 V) and (+1.1, +0.1 V) steps. This suggests that the charged state difference of the gold surface is not the main reason of the asymmetry.

It is known that ionic multilayers are spontaneously formed in the EDL of the electrochemical interface of ILs¹¹⁻¹⁸ and of electrolyte solutions of tetraalkylammonium hydroxides,⁶⁰⁻⁶² in the latter of which the formation of such structure was reported to be very slow, on the order of min. The mass transfer of ions in the ionic multilayers is expected to be slow compared with that in bulk. In fact, a study using surface force apparatus⁶³ found slow lateral dynamics of ions at IL|mica interface compared with that in bulk. MD studies on IL|electrode interfaces also found the slow in-layer dynamics of ions at the bottommost layer in ionic multilayers and, furthermore, illustrated that the inter-layer diffusion is significantly slower than the in-layer diffusion.⁶⁴⁻⁶⁶ The ultraslow relaxation found in the present SPR study is probably attributable to be slow inter-layer motion of ions in the ionic multilayers proposed by the MD studies. In addition to the ultraslow relaxation, we found the prominent asymmetry of the relaxation time to the potential-step directions. A plausible reason for the asymmetry is a interaction between gold and ions (TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$). Atkin and coworkers demonstrated, by using atomic force microscopy at IL|Au(111) interface, that the force required to rupture the bottommost ionic layer depends on the cations constituting ILs.⁶⁷ Their results indicate that the interaction of IL-constituting ions with gold varies with the ions. MD studies also confirmed the difference in the diffusion coefficients and the

adsorption free energies for cations and anions at IL|electrode interface.^{64,66} In fact, ESPR studies for several ILs shows that the asymmetry of the relaxation time depends on the ILs.⁴⁷ Further systematic ESPR studies at IL|gold interface for various ILs will reveal the details of the ultraslow relaxation and the interaction of ions with gold depending on ions, and such a study is in progress in our laboratory.

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Table 1: Parameters obtained from the fitting of the log-normal model to the potential-step transients of the SPR for [TOMA⁺][C₄C₄N⁻]||gold interface.

Potential step	$\log(\tau_0/s)$	σ	$\Delta\theta_{\text{slow}}$ (mdeg.)	$\Delta\theta_{\text{fast}}$ (mdeg.)
-0.3 to +0.7 V	2.40±0.47	1.23±0.22	+61±15	-40±15
+0.7 to -0.3 V	0.29±0.65	1.09±0.44	-44±14	+31±19
-0.1 to +0.9 V	2.82±0.67	1.47±0.51	+47±13	-31± 1
+0.9 to -0.1 V	1.25±0.21	1.49±0.46	-26± 8	+17± 6
+0.1 to +1.1 V	3.30±0.36	1.88±0.05	+38± 6	-17± 1
+1.1 to +0.1 V	1.27±0.09	1.04±0.27	-10± 3	+12± 3

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Figure captions

Fig. 1 (a) Cyclic voltammogram at the [TOMA⁺][C₄C₄N⁻]/gold interface at 50 mV/s. Time course of (b) the potential and (c) SPR angle shift during the potential step measurements.

Fig. 2 (a) Fitting results for the positive potential step (open circle, $0 \leq t/s \leq 300$ in Fig.1c) and the negative potential step (open square, $300 \leq t/s \leq 600$ in Fig.1c). The dotted lines and the dashed lines are fitted curves for the single exponential model and the log-normal model, respectively. (b) Distribution function for the positive (right) and the negative (left) potential steps from the fitting results.

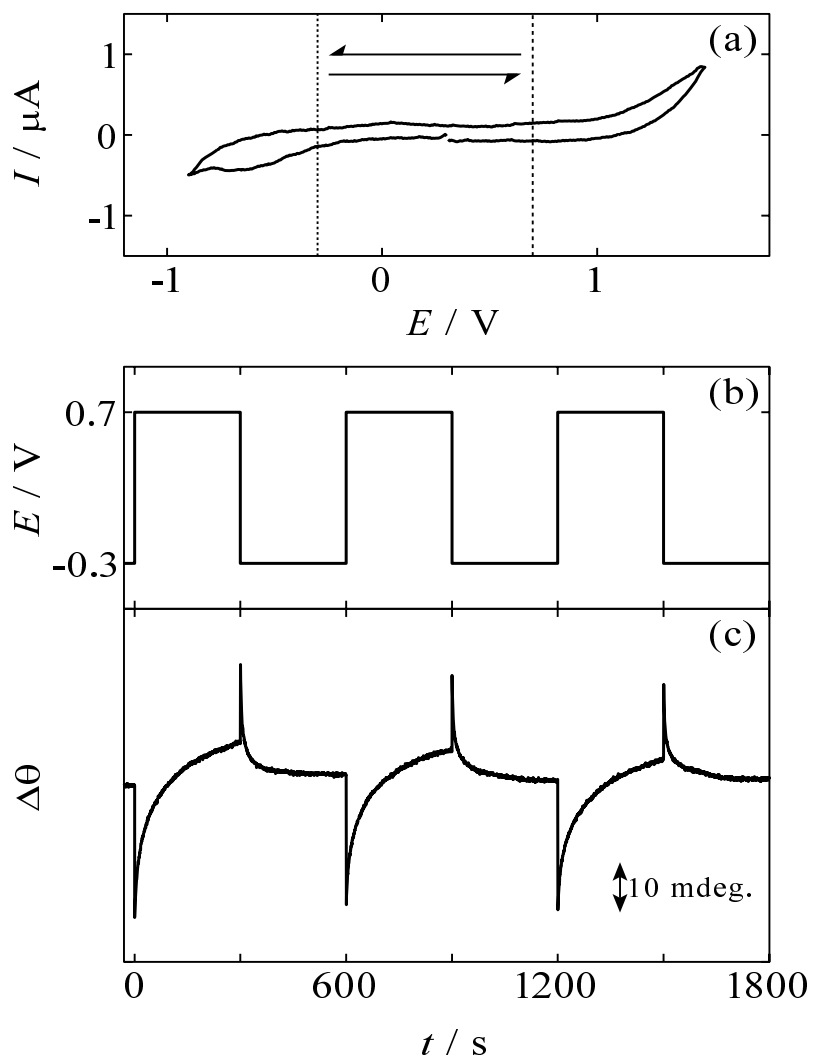


Fig.1 (Nishi et al.)

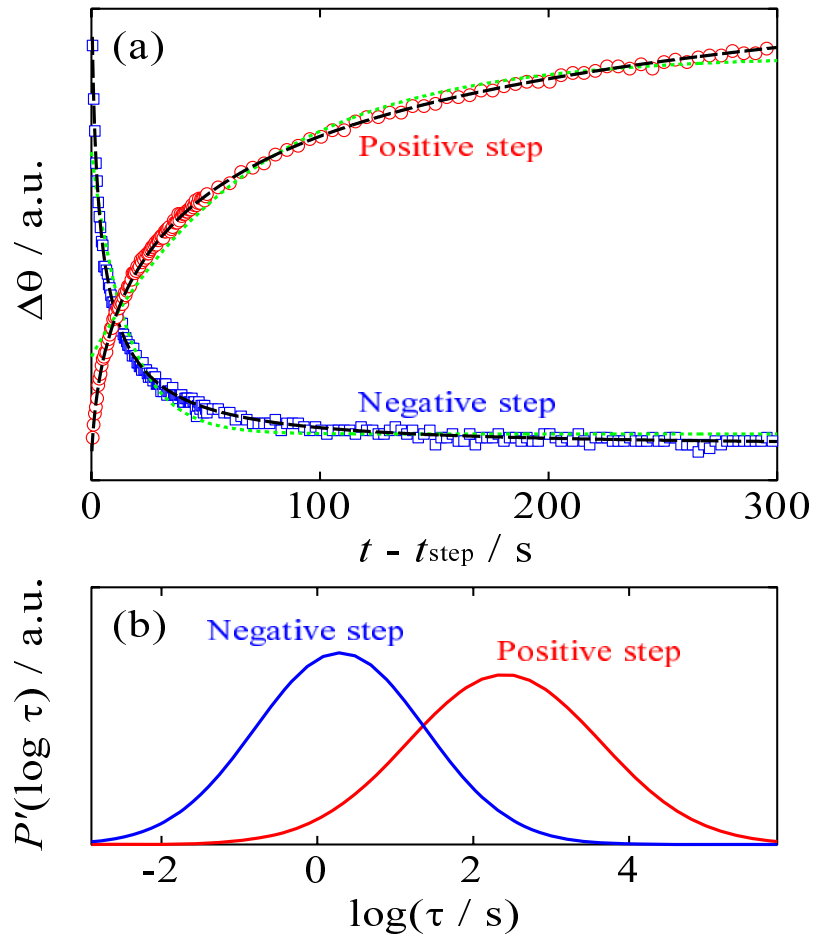
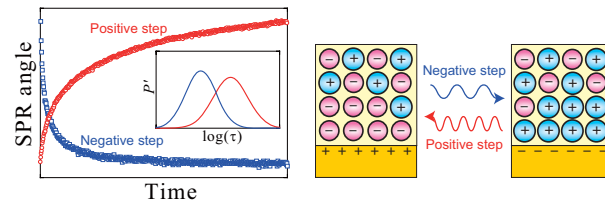


Fig.2 (Nishi et al.)

Tables of contents entry

Electrochemical surface plasmon resonance probes ultraslow relaxation of the structure at the ionic liquid|gold electrode interface and detects asymmetry of the relaxation time to the potential-step direction.

Asymmetry in ultraslow relaxation



ARTICLE INFORMATION

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Title: Ultraslow relaxation of the structure at the ionic liquid|gold electrode interface to a potential step probed by electrochemical surface plasmon resonance measurements: asymmetry of the relaxation time to the potential-step direction

Electronic Supplementary Information

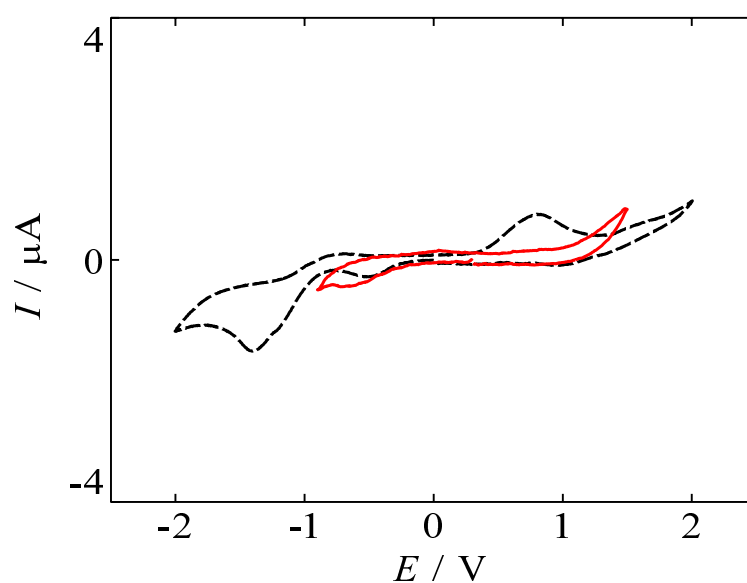


Figure S1: Cyclic voltammograms at the [TOMA⁺][C₄C₄N⁻]|gold interface for the capacitive potential region at 50 mV/s (red solid line) and for the potential window at 20 mV/s (black dotted line).

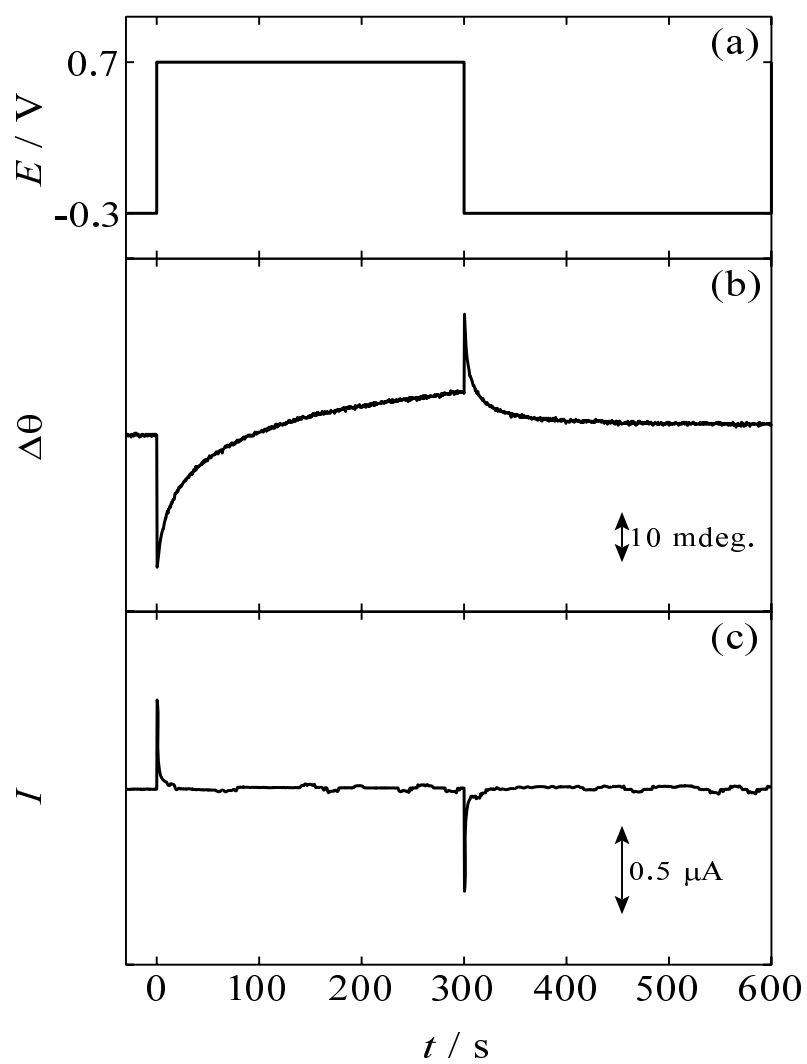


Figure S2: Time course of (a) the potential, (b) SPR angle shift and (c) the current during the potential step measurements.

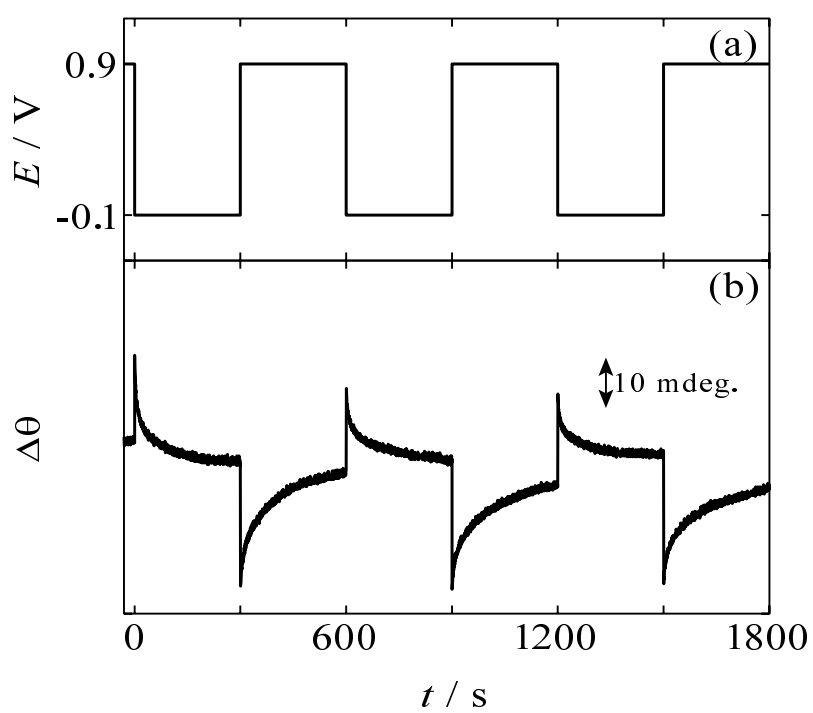


Figure S3: Time course of (a) the potential and (b) SPR angle shift during the potential step measurements between +0.9 and -0.1 V.

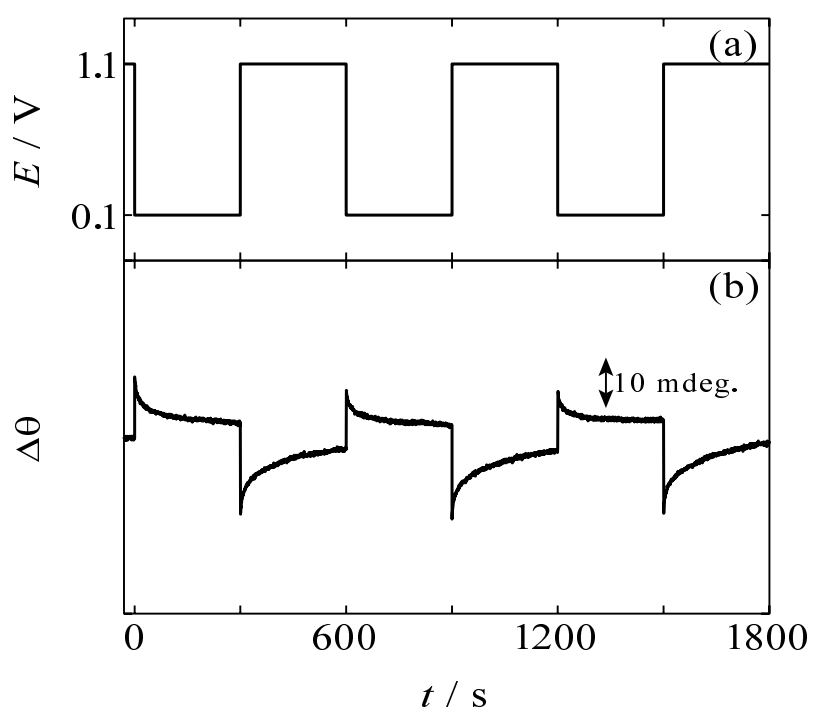


Figure S4: Time course of (a) the potential and (b) SPR angle shift during the potential step measurements between +1.1 and +1.1 V.