Surface pK_a of Amine-Terminated Self-assembled Monolayers Evaluated by Direct Observation of Counter Anion by FT-Surface Enhanced Raman Spectroscopy

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The acid–base reaction of aminoethanethiol (2AT) and 6-amino-1-hexanethiol (6AT) self-assembled monolayers (SAMs) on a gold electrode was monitored by Fourier-transform surface enhanced Raman spectroscopy (FT-SERS). A band attributed to counter anions, such as ClO_4^- or NO_3^- for NH_3^+, was clearly observed during protonation of the amino group of 2AT or 6AT. The band intensity decreased with increasing solution pH. The surface pK_a's of the 2AT and 6AT SAMs on a gold electrode at 0 V vs Ag|AgCl (saturated KCl) were 5.0 ± 0.2 and 3.8 ± 0.3, as evaluated from the intensity–pH curve.

As bis(4-pyridyl) disulfide modified gold electrodes are known to promote cytchrome c electrochemistry,[1] the surface electrochemistry of self-assembled monolayers (SAMs) of various thiols and sulfides on gold electrodes has been actively studied as potential functional modified electrodes.[2] In particular, SAMs with functional groups such as amino, carboxyl or pyridine groups, are utilized to control the promoter function[1] or immobilize other functional groups.[2] Evaluating the surface pK_a values of the functional group in the SAM is therefore important, however, the surface pK_a of SAMs generally differ from those in the bulk phase. Several methods such as contact angle,[3] capacitance,[4] quartz crystal microbalance (QCM),[5] infrared spectroscopy,[6] and SERS[7] have been employed to determine surface pK_a values.

SERS is one of the most powerful techniques[8] for studying the structure and structural change in SAMs induced by redox reactions, even though SERS has certain disadvantages in that the spectra are difficult to interpret, and oxidation and reduction cycle (ORC) treatment is required in order to obtain spectra with high signal-to-noise ratio. SERS is particularly useful for detecting stretching bands of typical inorganic anions such as ClO_4^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}, which are typical supporting electrolytes in electrochemistry. Recently, the present authors reported the redox-induced incorporation of ClO_4^- into 8-ferrocenyloctanethiol (8FT) SAM at a gold wire electrode observed by *in situ* FT-SERS.[9]

In the present paper we report the acid–base properties in amine-terminated SAM determined by FT-SERS. Various methods have been reported for obtaining the surface pK_a of amine-terminated SAMs,[3–7] however, the acid–base reaction monitored by detecting ClO_4^- or NO_3^- as a counter anion for the ammonium group has not been reported to the best of our knowledge. Such an approach is expected to provide information of regarding the electrical double layer and the complex formation constant at the surface, as SERS is able to detect several kinds of counter anions simultaneously.

Aminoethanethiol was purchased from Tokyo Kasei Co., Ltd., and 6-amino-1-hexanethiol, hydrochloride was kindly provided by the Dojin Chemical Co., Ltd. (Kumamoto, Japan) and used without further purification. A gold wire (1 mm diameter) polished with 0.3 μm Al_2O_3 powder was used as the working electrode. The surface was roughened by ORC to activate the surface for SERS by potential scanning 40 times between −0.2 V and 1.2 V in a 0.1 M (mol dm^{-3}) KCl aqueous solution.[9] A platinum wire and Ag/AgCl (saturated KCl) electrode were used as a counter and reference electrodes, respectively. All potentials in this paper are referred to the Ag/AgCl electrode. FT Raman and SERS spectra were recorded using a Bio-Rad FTS-175c spectrophotometer equipped with a Raman accessory unit. The gold electrodes were modified in a 20 μM 2AT aqueous solution for 20 min or 100 μM 6AT ethanolic solution for 5 min. The electrodes were then rinsed with pure ethanol followed by pure water (Milli-Q) to remove any excess modifier. All measurements were carried out at room temperature (25 ± 1 °C).

Figure 1 shows the FT-Raman spectra of (a) 2AT powder, (b) 1.0 M $HClO_4$, and (c-e) FT-SERS spectra of the 2AT SAM on a gold electrode at 0 V in solutions of 0.25 M $NaClO_4$ at several pH. In Figure 1(a), C–H stretching, N–H stretching bands can be seen, but the band at 933 cm^{-1} attributable to Cl–O stretching[10,11] is only seen in Figure 1(b). The SERS spectrum of the 2AT SAM at pH 2.6 is shown in Figure 1(c), where the 933 cm^{-1} is sharp and

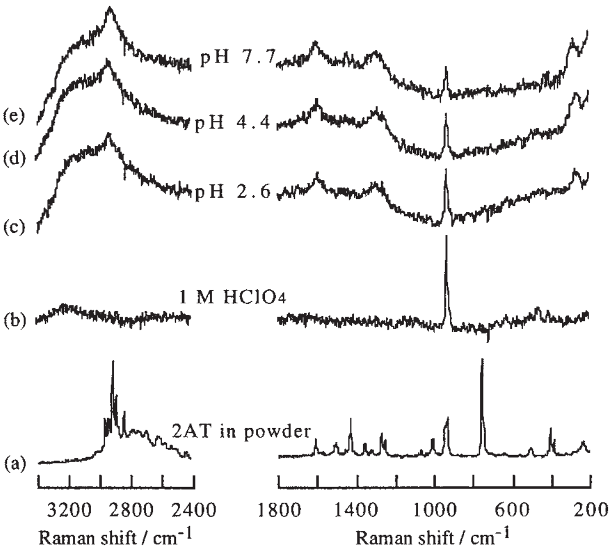

Figure 1. Raman spectra of (a) 2AT in powder and (b) 1.0 M $HClO_4$ aqueous solution, and SERS spectra of 2AT SAM on Au electrode at 0 V in (c) pH 2.6, (d) pH 4.4, and (e) pH 7.7 of Britton & Robinson buffer containing 0.25 M $NaClO_4$.

distinct. This band corresponds to the Cl–O stretching of ClO_4^-, indicating that the counter anion for the protonated 2AT SAM was detected clearly by FT-SERS as has already been achieved for oxidized ferrocene-terminated alkanthiol SAM in an aqueous $NaClO_4$ solution.[9] As the Cl–O stretching band is inactive in infrared (IR) spectroscopy, the detection of the ClO_4^- as a counter anion, which is one of the most frequently used anions in electrochemistry, is a distinct feature for Raman spectroscopy. The SERS intensities at 1300, 1610, and 2940 cm^{-1} were independent of pH, whereas the intensity of the 933 cm^{-1} peak decreased with increasing pH (compare Figure 1c and 1e), and became constant over pH 8.0. Similar experiments using mercaptoethanol, ethanethiol and propanethiol SAMs were also carried out, but no Cl–O bands were observed in any of the cases examined. The pH-independence of the 2940 cm^{-1} band intensity was a common feature of all these SAMs.

As the enhancement factor for SERS is sensitive to surface conditions, the intensity of the 2940 cm^{-1} band, attributed to C–H stretching, was used as an internal criterion, assuming that the C–H stretching intensity and configuration of the 2AT molecule were independent of pH. Figure 2 shows the normalized intensity (I_{933}/I_{2940}) vs. pH curves for the 2AT SAM at different electrode potentials, where I_{933} and I_{2940} represent the SERS intensity at 933 cm^{-1} and 2940 cm^{-1}, respectively. At a potential of 0 V, the surface pK_a of the 2AT SAM was 5.0 ± 0.2, which is in good agreement with the value obtained by double-layer-capacitance titration.[4b] The surface pK_a determined by our method was found to vary according to the electrode potential; at 0.1 V electrode potential, the pK_a shifted to 4.1 ± 0.2, and at 0.2 V, the pK_a became 3.4 ± 0.2. The effect of electrode potential on the surface pK_a of carboxyl-terminated alkanethiol SAM was studied in terms of capacitance[4b] and QCM.[5b] The direction of pK_a shift was found to follow the polarity of potential applied, which is thought to indicate that the pK_a shift for 2AT SAM is caused by local cation concentration.[5b]

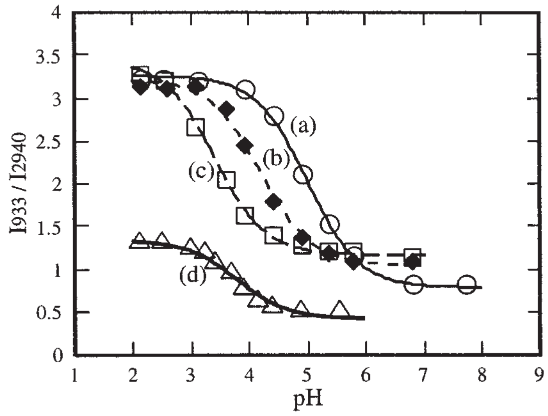

Figure 2. Plots of I_{933}/I_{2940} vs. pH. Normalized Raman intensity was obtained from SERS spectra of 2AT SAM on Au electrode at (a) 0 V (○), (b) 0.1 V (◆), (c) 0.2 V (□), and (d) 6AT SAM at 0 V (△).

The intensity at the Cl–O stretching band weakened with increasing alkyl chain length for the amine-terminated alkanethiol SAM. The surface pK_a of the 6AT SAM was 3.8 ± 0.3, smaller than that of the 2AT SAM by ca 1.2 unit. The surface pK_a of aminodecanethiol (10AT) SAM was not evaluated due to a low signal-to-noise ratio at 933 cm^{-1}.

Similar experiments were conducted using 0.25 M $NaNO_3$ in order to assess the effect of the anions used. In the SERS spectrum for 2AT SAM in a 0.25 M NO_3^- solution at pH 2.6, a strong band at 1048 cm^{-1} was observed, attributed to N–O stretching.[10] The intensity of the N–O stretching band in solution was ca. 80%[9] of that of the Cl–O band of ClO_4^-, and decreased with increasing pH. The pK_a value evaluated from the curve was 5.0 ± 0.2, almost identical to that for ClO_4^-. These results indicate that the pK_a of 2AT SAM at 0 V is independent of the anions used. In addition, both the Cl–O and N–O stretching bands were clearly observed in the SERS spectrum of 2AT SAM in a mixed solution of 0.25 M $NaNO_3$ and 0.25 M $NaClO_4$, and the intensity ratio reflected the component ratio in the solution, indicating that the interaction between the protonated 2AT and NO_3^- was almost equal to that for ClO_4^-.

In conclusion, the surface pK_a's of 2AT and 6AT were evaluated by *in situ* FT-SERS measurements. This method is a useful technique for detecting counter anions or determining the surface pK_a for SAMs with cationic functional moieties.

References and Notes

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